Modeling Droplets And Emulsions With Insoluble Surfactant

Flowing Through Complex Environments

by

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Abstract

Multiphase flows are so common in everyday life as to go unnoticed, yet they have eluded rigorous characterization, especially in confined settings and under the influence of surfactant. The objective of the present work is two-fold: (1) to develop high-accuracy and extensible computational tools to study confined and contaminated emulsions, and (2) to elucidate new physics that remain difficult or impossible to probe using other experimental or numerical techniques. Mathematical formulations and numerical algorithms are developed in the context of the boundary-integral method, and applied to a wide range of systems and fluid properties, including droplets interacting with fibrous and non-axisymmetric particles, and high-density contaminated emulsions flowing through a porous medium.

A boundary-integral formulation is introduced that enables droplets to interact with arbitrary smooth surfaces in tight-squeezing conditions. The behavior of droplets flowing between and around cylindrical particles is simulated, with respect to capillary number, viscosity ratio, drop size and solid-particle aspect ratio. Flow rectification is demonstrated for constrictions that are nonsymmetric with respect to flow reversal. The internal circulation within droplets is analyzed as a dynamical system and visualized by introducing an algorithm for the 3D advection of a ‘material surface’ with an arbitrary boundary. While regular flow is predicted within drops trapped between two cylindrical particles, chaotic advection within drops trapped in a three-sphere constriction suggests superior mixing properties.

The interfacial behavior of surfactant-laden drops squeezing through a three-sphere constriction is considered. Sharp surfactant-concentration gradients form during various stages of the squeezing process. Even a low degree of contamination significantly decreases the critical capillary number for droplet trapping. Increasing the degree of contamination affects surface mobility and further decreases the critical...
capillary number as well as drop squeezing times, up to a threshold above which the addition of surfactant negligibly affects squeezing dynamics. Finally, a high-density emulsion squeezing through a periodic array of spheres is considered. Away from critical squeezing conditions, the presence of surfactant increases squeezing times, while the inverse correlation is observed near the critical capillary number.
to my parents, Mom & Pops
Acknowledgements

My mom, an Icelandic sheep farmer, still boggles at the concept of me sitting in front of a computer screen all day, every day. My dad once wondered that I was being paid to simulate objects, which even if they were real, would be too small to see. It is difficult to convey to them, that anything I accomplish is due less to my affinity for science, and more to a lifetime of being convinced that I could do well at anything I try. Thanks for that.

On another familial note, impressively frequent visits, and invitations to visit, from brothers and parents have been critical to the buoyancy of my mental state. Various brothers have fixed my car and/or driven me across the country several times. There have been attempts to photograph black bears in the Flatirons, sight manatees in the Everglades, and even occupy a pickup-truck-turned-tiny-house in the middle of grizzly-country Montana (with only this last one being unarguably successful).

Several other people were noteworthy causally in the existence of this oversized treatise. Though I doubt she recalls the conversation, I would like to thank my undergraduate adviser Dr. Karen Winey for, upon realizing how interested I was in pursuing research, encouraging me to apply to Ph.D. programs (being so supportive at that time in my career certainly required a dose of optimism!). I would like to thank the support of the new Materials Science Program at CU Boulder and specifically Dr. Christopher Bowman, for shoring up my resolve as I jittered around the world of molecular dynamics before landing in the field of computational fluid dynamics (with hardly a simulated splash!). I would to thank all my groupmates throughout the years, including Rocio Navarro and Gesse Roure for a pleasant work environment and stimulating discussions.

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to increasing periods of motion 3.63, 4.05, and 4.43, respectively. (b) Evolution of surfactant
concentration with respect to contamination. For direct comparison, \(\Gamma_{max}\) is scaled by \(\beta\)
and shifted by \((\beta \Gamma_{max})_{eq}\).

5.6 Squeezing behavior and surfactant distribution for a lower-density emulsion \((c_{em} = 0.36)\)
flowing through an array of spheres \((Ca = 0.995, \beta = 0.05, \lambda = 4)\). The period of motion is
\(T = 2.79\).

5.7 Drop- and emulsion-phase velocities for the moderate-density emulsion flow \((c_{em} = 0.36)\)
pictured in figure 5.6 \((Ca = .995, \beta = 0.05, \lambda = 4)\).

5.8 Very-near-critical squeezing of a moderate-density emulsion \((\beta = 0.05, \lambda = 1, c_{em} = 0.36)\). (a)
Away from critical, a linear relationship between \(Ca\) and \(1/T^3\) is observed, however, deviations
from this relationship occur very near to critical conditions. (b) Very near critical squeezing
conditions, the drop phase moves slower than the continuous phase for the majority of the
squeezing cycle \((T = 7.55, Ca = 0.43)\). (c) Snapshots of drop squeezing for the near-critical
\(Ca = 0.43\). The surfactant is swept to the downstream half of the drop during part of the
squeezing cycle \((t_T = 3.88, \text{ shown from a different angle to reveal surfactant distribution})\).
Chapter 1

Introduction

One thing I can guarantee you. You may not be a great deal wiser from my talk today, but you will be a great deal older.

-Melvin Helitzer

1.1 Why are slow-moving fluids important, and why use computers to study them?

Cooking became slightly more entertaining to me after learning about multiphase fluids. One day I was preparing quinoa, which is a small almost-spherical seed, by dumping a box of it into a pot of water (one fluid phase) and oil (another fluid phase). As the quinoa settled through the fluids, it broke the oil into small droplets that then rose through the dense layer of seeds. This is an example of an emulsion (oil-in-water) flowing through a porous media (a bunch of granular particles).

Later, I had to wash the dishes, using soap. Soap has been in use since 2800 BC, more than four and a half thousand years before the idea of the atom became mainstream. Household soap is a surfactant, a molecule that consists of one small part that is water-loving, connected to a long chain of atoms that severely dislikes being in contact with water. When you add surfactants to a multiphase fluid, they will try
to find a way to satisfy both requirements: at the interface of oil and water, for instance, the hydrophilic part can be contentedly surrounded by water molecules while the hydrophobic tail extends into the oil. The properties of this oil-water interface change in the presence of surfactant, as is to be expected when adding new components to any system: specifically, surfactants decrease the surface tension between the fluids. Surfactants are everywhere (for example, the most distinctive chemical component of raw quinoa is saponin, a surfactant), and they are quite effective at disrupting lipid membranes, such as those of viruses, as well emulsifying oil in water to effectively clean the dishes.

Besides domestic use, a number of other industries have come to rely heavily on surfactants in the presence of slow-moving or highly-confined fluids. Enhanced oil recovery uses surfactant to increase the yield of oilfields. In this case, oil (petroleum) and water again form the two phases of an emulsion, and a subsurface setting of sandstone or limestone is the porous medium. Historically, and to this day, much research on the properties of confined emulsions has been with a subsurface setting in mind, and many open questions as well as results within this dissertation are presented in that context as well. Other important industries and applications that make use of confined, multiphase flows include microfluidics, textiles, food and beverage, and pharmaceuticals.

Despite their prevalence, the physics of droplet flows interacting with solid surfaces has remained difficult to characterize, particularly in the presence of surfactant. Many fundamental questions remain under active investigation. What is the apparent viscosity of emulsions as a function of the properties of the emulsion and the porous media? What are the pore-scale mechanisms that affect droplet transport? And, how does the presence of surfactant affect these questions? From an experimental standpoint, the fact that solids tend to be either opaque or refractive makes it difficult to observe and record fluid flow with high resolution. Similarly, the concentration of surfactant, which often consists of a less-than-maximally-packed single layer of molecules, it very challenging to measure. Much experimental work has been invested and progress made in overcoming these limitations, which is outlined in the introductions of the following chapters. The above difficulties are essentially nonissues when it comes to simulations, considering that the fluid velocities and positions and surfactant concentrations are precisely the quantities being calculated. The resolution offered by simulations is one of their main benefits, along
with their reduced cost and ability to isolate the parameter space (i.e., hold one value exactly constant, while varying another). Finally, computational fluid dynamics (CFD) has achieved such widespread success because the Navier-Stokes equations are an impressively predictive model.

The equations that govern fluid flow, the Navier-Stokes equations, have famously yet to be ‘solved.’ Even when mathematicians eventually label them as either ‘solved’ or ‘unsolvable,’ that breakthrough is unlikely to have a much of an impact on the field of computational fluid dynamics. For example, as discussed in the following section, all the computational work herein actually uses a simpler version of the equations, the Stokes equation, that is rather definitely ‘solved.’ The difficulties, which prevent analytical solutions, arise when you have multiple flows interacting with each other and with solid phases, and you add in the coupled effects of additional physical phenomena, such as those of surfactant. The Navier-Stokes equations ‘simplify’ the movement of a real fluid by averaging over the motion of all of its individual molecules, and treating fluids as a continuous material (i.e., a ‘continuum’). However, in order to use computers to simulate fluids, the assumed-continuous fluid must be converted into a discrete formulation, the only type of math that current computers understand. In many cases, the discrete nature of the formulation is most concerning systematic source of error in CFD, as opposed to any shortcoming of the Navier-Stokes equation or other physical assumptions, and therefore care must be taken to ensure convergence of results with respect to the resolution of the simulation. Fundamental progress in simulating fluid flow is beneficial not only for its physical predictions, but also for the utility of the developed numerical algorithms and the advances in applied math.

The goal of this dissertation is to answer fundamental questions about the behavior of droplets interacting with complex environments, and to investigate how surfactant affects this behavior. This objective is attacked with the tool of computer simulation, by developing versatile and robust numerical algorithms to enable several new classes of droplet flows to be modeled with high fidelity. For the entirety of this work, the boundary-integral method (BIM) is used. BIM is known most for its high accuracy and resolution of interfacial behavior, due to the fact that the position and dynamics of interfaces are explicitly calculated. An algorithm is introduced to enable droplet interaction with arbitrarily-shaped particles, which was previously untenable due to the highly singular behavior of BIM integrals when two interfaces
approach each other. A new method to visualize the internal flow of droplets is developed. A robust algorithm for surfactant transport on a tight-squeezing droplet is formulated, and then implemented to study periodic emulsions squeezing through porous media. The remainder of this chapter briefly introduces the fundamental mathematics and physics, summarizes the work that served as the foundation for this dissertation, and then summarizes the content of this dissertation.

1.2 Deriving the Stokes Equation

If you zoom out far enough, the Earth simplifies to a blue marble, and the solar system does not notice whether I turn left or right out of CU Boulder’s parking lot every day. Zoom back in, and you discover that a number of a smaller objects (for example, actual blue marbles) are being carried around the Earth’s orbit. Zooming in further on an actual blue marble, we find that it is composed of atoms, but this fact is not something that complicates children’s games. They are sufficiently zoomed out to care only that the marble bounces and rolls in a predictable fashion, specifically that a marble in motion tends to remain in motion (Newton’s first law), and that its acceleration is directly proportional to how hard it is pushed, divided by its mass (Newton’s second law).

Fluids also consist of atoms, but for most of our (numerous) daily interactions with them, we can pretend they are continuous entities. This does not exempt them from Newton’s laws. The movement of a marble is fairly easy to picture, but how to describe the motion of a continuum? Even a small piece of a continuously-deformable substance is still very zoomed out compared to an atom, and is often imagined as a simple cube, albeit one with ball joints at each of its corners, and whose edges can be stretched. This cube (in fluids, often referred to as a fluid parcel or fluid element) must be placed somewhere, so let one of its corners be fixed in space, and let us attach a handle to each of the three faces not connected to the fixed corner. We can now deform our cube arbitrarily by pushing or pulling on our three handles. If we push or pull perpendicularly to a face, we are applying pressure to the cube. If we push or pull parallel to a given face, we are exerting shear on the cube. How strongly the cube resists our efforts to shear it depends on how quickly we are trying to strain it: this proportionality factor is its viscosity. Considering the three
handles can be moved in three independent directions in 3D space, their effect on our cube can be encapsulated in a mathematical object that contains nine values. This object is known as the Cauchy stress tensor, symbolized by

$$\Pi = -p I + 2\mu E$$  \hspace{1cm} (1.1)

where $\Pi$ is known as the (second-order) Cauchy stress tensor, $p$ is an isotropic pressure (all three pressure terms are assumed equal due to liquid properties being independent of orientation), $I$ is the identity tensor, $\mu$ is viscosity, $E = \frac{1}{2} (\nabla u + (\nabla u)^T)$ is the rate-of-strain tensor, and $u$ is velocity. Note that $E$ is symmetric (ultimately related to the conservation of angular momentum), reducing the independent elements of the stress tensor to four. Now that we have a picture of how small pieces of fluid respond to pushing and pulling, we can plug this stress tensor into a general equation for momentum transport, valid for any continuum, known as the Cauchy momentum equation,

$$\rho \frac{Du}{Dt} = \nabla \cdot \Pi + f$$  \hspace{1cm} (1.2)

where $\rho$ is the fluid density, $D/Dt$ is the material derivative and $f$ is a catch-all for external body forces, e.g., gravity.

We are now almost in a position to derive the Navier-Stokes equation, a nonlinear partial differential equation that describes fluid flow, and one of the more successful and widely-used equations in engineering. But before that, several simplifying assumptions should be mentioned, which are possible because we are interested in a specific class of simple multiphase fluids. First, a constant value for viscosity is possible due to the assumed linear relationship between strain rate and shear stress: this is the definition of a Newtonian fluid. Second, the fluid is assumed to be purely viscous (like honey, oil, and water), as opposed to viscoelastic, as is often a property of polymers. In addition, we assume that the fluid is able to exactly match any isotropic pressure exerted on it: this is the definition of an incompressible fluid. Incompressibility is common for liquids as a result of their molecules naturally ordering themselves into the densest possible configuration (or ensemble of configurations), and adds an additional constraint on their
behavior. Starting from the continuity equation, which simply enforces conservation of mass,

\[
\frac{1}{\rho} \frac{D\rho}{Dt} + \nabla \cdot \mathbf{u} = 0 \tag{1.3}
\]

and noting that density remains constant for incompressible fluids, we arrive at \( \nabla \cdot \mathbf{u} = 0 \) for incompressible fluids. So, plugging (1.1) into (1.2) and enforcing incompressibility results in the constitutive equations:

\[
\rho \frac{Du}{Dt} = -\nabla p + \mu \nabla^2 \mathbf{u} \quad \text{(Naver-Stokes Equation)} \tag{1.4}
\]

\[
\nabla \cdot \mathbf{u} = 0 \quad \text{(incompressibility constraint).} \tag{1.5}
\]

Finally, we can make one more simplification because our fluids of interest are moving slowly (compared to the length scale of interest). A useful and prevalent tool in fluids mechanics is the dimensionless number. Parameters that do not rely on specific units allow for succinctly describing fluid-property relationships in a general yet quantitative manner. Systems that are described in specific units can be similarly nondimensionalized and their behavior predicted. Perhaps the most famous nondimensional number is the Reynolds number: the ratio of inertial to viscous forces determines whether the flow will be laminar or turbulent, and is symbolized as

\[
Re = \frac{\rho VL}{\mu} \quad \text{(Reynolds number)} \tag{1.6}
\]

where \( V \) is the magnitude of a characteristic velocity, and \( L \) is a characteristic length.

For many real-world examples of fluidic systems, such as microfluidic devices and other highly-confined environments, biological flows, and highly-viscous fluids, it is safe to approximate the Reynolds number as exactly zero (i.e., inertial forces are zero). Fluid behavior at \( Re = 0 \) is known as the Stokes regime and results in one final simplification of the Navier-Stokes equation. The first term in (1.4) encapsulates the effect of inertia, so setting this to zero results in the Stokes equation,

\[
-\nabla p + \mu \nabla^2 \mathbf{u} = 0 \quad \text{(Stokes Equation).} \tag{1.7}
\]
Rather critically for the existence of boundary-integral methods, this final simplification removes the nonlinear terms of the Navier-Stokes equations, resulting in a linear Stokes equation. The linearity of the Stokes equation allows for the superposition of solutions. The details of constructing and implementing general boundary-integral methods can be found in *Boundary Integral and Singularity Methods for Linearized Viscous Flow* (Pozrikidis, 1992). Zero-Reynolds number (Stokes) flows can behave in a manner that is often counter-intuitive to everyday experience. If you abruptly remove the pressure gradient driving a single-phase Stokes flow, all motion within that fluid will instantly cease (i.e., the flow is ‘instantaneous’). Stokes flow is also time-reversible. In a classic example, G.I. Taylor demonstrates that a blob of red dye, placed in another high-viscosity fluid between two concentric cylinders, can be stretched to near-invisibility when the interior cylinder is rotated, only to return to its original shape when the cylinder is rotated back. However, much of this traditional Stokes-flow wisdom does not hold for multiphase systems when the dissipative effects of surface tension are involved. For example, consider a single droplet being squeezed by an extensional flow, where all fluids are in the Stokes regime. If you abruptly remove all body forces, the droplet will subsequently relax into its minimal surface (a sphere). Clearly, such flows are neither instantaneous nor time-reversible. Indeed, the overall rheology of emulsions is generally nonlinear.

### 1.3 General surfactant physics

Surfactants locally decrease the surface tension of a fluid-fluid interface, corresponding to an increase its ability to be deformed. For example, after adding a uniform concentration of surfactant to the surface of a droplet, less force is required to squeeze it out of its preferentially-spherical shape. However, surfactants are swept along with the flow at the droplet interface, so droplets can quickly develop non-uniform surfactant distributions (especially considering that the diffusivity of surfactant molecules is typically very low). The deformability of the interface is not restricted to bending motion, it can also be stretched, and surfactants also increase this type of deformability. For example, when only half of a droplet is covered in surfactant, the half without surfactant pulls harder in a direction tangential to the interface, inducing a flow along the surface. This phenomenon is known as the Marangoni effect, the additional
surface-tangential stresses are called Marangoni stresses, and the induced flow is the Marangoni flow. The phenomenon was discovered by Prof. James Thomson.

Thomson first noted the Marangoni effect by solving the mystery of ‘tears of wine’ in 1855. The continuous formation of droplets above the surface of a high-alcohol-content wine in a open glass is ultimately caused by the higher surface tension of water as compared to alcohol. After a thin film of wine has risen up the side of the glass to due capillary forces, the alcohol evaporates, and the higher surface tension of water pulls more liquid upward until a droplet forms. Since then, the Marangoni effect has on occasion caused confusion in the world of fluids. Small droplets sedimenting in the Stokes regime were found to have a settling velocity matching that predicted for a hard sphere, instead of a fluid droplet. The disparity was eventually attributed to the presence of trace surfactant, which immobilizes part of the drop interface due to Marangoni stresses. Out of four ‘unsolved problems in classical mechanics’ currently listed on Wikipedia, one is upstream contamination. One day in 2008 while preparing mate, a South American beverage similar to tea, a Argentinian graduate student noticed that mate leaves ended up in the container from which clean water had been poured. The ability of contaminants to climb up a waterfall of up to 1 cm was later attributed to Marangoni effects: mate tea leaves are high in stearic acid, a surfactant (Bianchini et al., 2013).

In the present work, the effect of surfactant on interfacial dynamics is most relevant when that interface is in close proximity to a solid surface. Consider a contaminated droplet interface approaching a flat surface, as shown in figure 1.1. There is a strong tendency for a dimple to form in the fluid interface in this case, even when approaching a curved surface or another deformable interface (Yiantsios & Davis, 1990). A lubrication layer of intervening fluid forms between the drop and the solid, which must begin to drain away as the drop continues to near the surface. This outflow of the intervening fluid includes the droplet interface itself, sweeping surfactant toward the edges of the near-contact region, and developing a gradient of surfactant concentration. Recall that, put simply, the Marangoni effect tends to restore non-uniform surfactant to a uniform distribution. So, the Marangoni stresses that develop resist the outflow and therefore slow the drainage of the lubrication layer.
CHAPTER 1. INTRODUCTION

Figure 1.1: Part of a surfactant-covered droplet is shown approaching a solid surface, after forming the dimpled interface characteristic of such interactions. The fluid between the droplet and the solid is forced outward as the lubrication layer drains, sweeping surfactant along with it. The gradient in surfactant concentration gives rise to resistive Marangoni stresses located on the droplet interface. The dashed black line emphasizes the symmetry of the system.

1.4 Foundational work

The advances outlined herein build from a series of breakthroughs by Zinchenko & Davis related to modeling droplets in the vicinity of solid particles, using the boundary-integral method. It was demonstrated in 2006 that freely-suspended droplets interacting with spheres and spheroids fixed in space can be stably modeled using the Hebecker density formulation for solid-particle contributions, together with a suite of desingularization tools (Zinchenko & Davis, 2006). The work was later extended to periodic and multidrop systems (Zinchenko & Davis, 2008b, 2013). To the best of the author’s knowledge, this remains the only method of attack that has been successful for using BIM to model emulsions squeezing through granular particles (as opposed to channel flow) near critical conditions. Alternative numerical techniques, such as the lattice-Boltzmann method, and related efforts by other research groups relevant to each topic herein are described in the introductions of respective chapters. Prior to the work presented herein, the capabilities of the Davis group’s CFD packages included simulating droplets interacting with spheroids or tori, clean emulsions flowing through porous media, and contaminated emulsions in the absence of a solid phase.
1.5 Dissertation overview

Several novel capabilities pertaining to the boundary-integral method are described in detail, and used to investigate the physics of droplets in complex environments and under the influence of surfactants. Chapter 2 details a new method to simulate drops squeezing through arbitrarily-shaped particles. This technique, termed the multimesh desingularization method, leverages both adaptive meshing and high-order singularity subtraction to remove fundamental limitations of the boundary-integral method. In addition, a fast semi-analytical method is developed for use with axisymmetric particles. Notably, high-accuracy results were obtained for drops squeezing through and around cylindrical particles, as a model for confined flow through fibrous materials. Even more complex-shaped particles were demonstrated to exhibit flow-rectifying behavior, allowing drops to pass more easily from one direction than another. The work has revealed the relevance of the Stokes paradox and lubrication layers for these instances of multiphase flow.

Chapter 3 considers the internal circulation and mixing within two steady-state trapped droplets, one trapped between three spheres and another between two capsules. Several techniques, including the convection of a bounded ‘material surface,’ are developed to visualize and quantify internal circulation within drops in creeping flow, provided only the interfacial velocity field. The internal velocity fields of both droplets are analyzed as dynamical systems. Interestingly, regular flow is observed within the two-capule droplet, while chaotic flow is predicted for the three-sphere droplet. A video was submitted to the 2019 APS DFD Gallery of Fluid Motion, titled *A creeping drop denied passage?*, which graphically explains some of these ideas (Gissinger et al., 2019b).

Chapter 4 describes a comprehensive investigation of the effects of surfactant on a single drop embedded in a far-field flow squeezing between three spheres. Despite the prevalence of surfactants in confined biological and subsurface settings, their influence on fluid interfaces under tight squeezing conditions had been largely uncharacterized. Of fundamental interest was the ability to predict how the presence of surfactant affects drop transport through constrictions with respect to degree of contamination and fluid properties, which was achieved with advanced numerical techniques. The ability of drop surface contamination to reduce droplet trapping (up to a point) was quantified, and several distinctive modes of
surfactant transport were related to specific combinations of fluid properties. For example, droplets can exit the constriction with a bimodal distribution of surfactant at sufficiently low viscosity ratios.

In chapter 5, the robust surfactant convection algorithm is implemented for a periodic emulsion flowing through a cubic array of spheres. In this case, the drop phase moves faster than the continuous phase (away from critical conditions), and the surfactant is swept to the back of the drop and remains confined to the trailing half for the duration of squeezing cycle. Qualitatively different surfactant behavior and squeezing trends are observed in this system, as compared to a single drop in far-field flow. For example, low degrees of contamination increase squeezing times in the case of periodic emulsions. In chapter 6, concluding remarks and suggestions for future research directions are provided.
Chapter 2

Drop squeezing between arbitrarily-shaped obstacles

This work has been submitted to the Journal of Fluid Mechanics with co-authors Alexander A. Zinchenko and Robert H. Davis.

A round man cannot be expected to fit in a square hole right away.

He must have time to modify his shape.

-Mark Twain

Synopsis

A fully three-dimensional boundary-integral method (BIM) is developed for the interaction of drops, suspended in a uniform far-field flow at small Reynolds number, with arbitrary Lyapunov surfaces. The close approach of fluid interfaces to solid surfaces poses significant challenges for numerical BIM implementations, due to the highly singular behavior of single- and double-layer boundary integrals. Two new methods are described that generalize the accurate calculation of the highly-singular surface integrals used by high-order desingularization techniques. The first method is semi-analytical, and applies to axisymmetric solid obstacles (in an arbitrary 3D configuration). An axisymmetric particle can be divided
into a series of characteristic disks along its axis, for which closed-form expressions for single and double layers are derived in terms of elliptic integrals. To accommodate arbitrary smooth surfaces, a multimesh desingularization method is introduced that calculates surface integrals utilizing a hierarchy of embedded mesh resolutions, together with distance-activated mesh interactions. Several particle shapes, including spherocylinders (capsules) and flat plates, are used to represent major classes characteristic of porous media. A droplet approaching a capsule will break up after forming two lobes, connected by a thin filament, on either side of the capsule. The cross-sectional shape of the filament affects lubrication behavior. A constriction made of two parallel capsules, even of low aspect ratio, significantly retards drop passage compared to two spheres. Trends in drop squeezing between two capsules are summarized over a range of capillary number, viscosity ratio, drop size and capsule length. A constriction of two coplanar plates results in notably different lubrication and squeezing behavior. Flow rectification is demonstrated for constrictions that are nonsymmetrical with respect to flow reversal, for several non-axisymmetric particles.

2.1 Multiphase flow environments are often complex

Emulsions are encountered in a variety of environments, such as multiphase flow through fibrous materials, packed beds with complex pellet shapes, and tortuous subsurface settings. Fields ranging from separations processes to oil recovery to microfluidics stand to profit from understanding of Stokes-flow droplet behaviour near complex surfaces. Efforts toward high-resolution microscale numerical models of nonwetting emulsions in complex environments have been stymied, chiefly due to the extremely close approach of fluid-fluid interfaces to solid surfaces. The intervening lubrication layer critically influences interfacial dynamics, making it difficult to use simplifying theory for these regions, while also presenting formidable challenges for numerical methods. To overcome some of these limitations, we introduce an extension to the boundary-integral method that leverages both adaptive meshing and high-order singularity subtraction to allow simulation of tight-squeezing drop motion between arbitrarily-shaped smooth solid surfaces.

Although a common model for porous media is an ensemble of spherical particles packed in space, several interesting classes of material fall outside this description, such as packed beds of pellets or
extrudates, fibrous material or experimental setups such as planar constrictions. Probing detailed flow behavior in such cases is difficult, but there is a growing focus on pore-scale resolution (Blunt et al., 2013). Experimental velocimetry methods, such as magnetic resonance or x-ray tomography (Huang et al., 2017; Al-Abduwani et al., 2005), for visualizing and quantifying confined flows are continually improving, strengthening the relationship with computational studies that can provide direct comparisons. For example, Zarikos et al. (2018) used particle-tracking velocimetry to track the interface as well as internal circulation of non-wetting drops as they are trapped and remobilized within porous media. Krummel et al. (2013) and Oughanem et al. (2015) investigated the recovery of trapped oil, based on capillary number and oil ganglia size distribution, and they were able to resolve individual drops using confocal microscopy and high-resolution micro-computed tomography, respectively. Using similar techniques, Pak et al. (2015) identified a new single-pore mechanism of drop fragmentation. Herring et al. (2013) demonstrate the dramatic effect that pore geometry has on the shape and connectivity of the nonwetting phase (e.g., see figure 9 therein). Typically these experiments involving porous media cover length scales beyond the reach of simulation, while resolving small-scale flow and interfacial behavior remains the territory of high-resolution numerical models.

Simulation techniques for large-scale multiphase systems include the lattice-Boltzmann, volume of fluid and boundary-integral methods, each of which occupy a niche within the field of computational fluid dynamics. Lattice-Boltzmann techniques represent a powerful simulation tool for large-scale flows interacting with complex boundaries; the following four examples utilized various lattice-Boltzmann methods to model the behavior of the nonwetting phase within porous media. Mantle et al. (2001) provide exact comparisons between magnetic resonance imaging results and lattice-Boltzmann simulations for Stokes flow in a packed bed of pellets, after scanning the experimental matrix and reconstructing it for their computer model. Pan et al. (2004) demonstrated the application of 3D lattice-Boltzmann methods to large-scale, confined multiphase flow between spherical particles or within spherical cavities. Hao & Cheng (2010) calculated the relative permeabilities of a packed-sphere bed, as well as that of carbon paper, modeled as a matrix of high-aspect-ratio fibers. They concluded that, for this anisotropic fibrous matrix, flow direction has negligible effect on the relative permeability. Finally, Yiotis et al. (2013) showed the
existence of several flow regimes depending on Bond number for liquid blobs within realistic 2D pore
structures. The volume of fluid method has also been used to model drop breakup when flowing between
cylinders, such as the 2D study of Dietsche & Neubauer (2009). Ardekani et al. (2009) used this method to
demonstrate that a drop may become perforated when pinched between two particles in shear flow. When
implementing any of these techniques, a persistent problem is precisely capturing the evolution of the
fluid-fluid interfaces, especially in the proximity of the solid phase. The boundary-integral method resolves
these interfaces explicitly, by reformulating the multiphase Stokes problem such that collocation points
need only exist on boundaries as pioneered by Rallison & Acrivos (1978). The deformation and
near-breakup of drops confined between parallel plates was simulated by Janssen & Anderson (2008a),
demonstrating drop breakup modes consistent with experiment. Zinchenko & Davis (2013) simulated many
(50-100) clean drops in pressure-driven flow through a bed of randomly packed spheres, including
treatment of cascading drop breakup.

The boundary-integral method (BIM) is a powerful tool for low-Reynolds-number flow, and utilizes
an integral formulation of the Stokes equations to explicitly resolve interfaces. BIM allows for efficient
calculation of interfacial motion at high orders of accuracy, but it comes at the cost of highly-singular
boundary integrals wherever two interfaces approach each other closely, as is certainly the case for
tight-squeezing drops. This formidable numerical issue is typically addressed with adaptive meshing (see
Kropinski (1999) for an example in 2D) or singularity subtraction techniques that rely on analytical
expressions for various contributions to the potential (Rallison & Acrivos, 1978). For example, Fan et al.
(1998) use a completed double-layer formulation to allow simulation of solid-sphere suspensions that can
approach each to within 5% of their radius. Zinchenko & Davis (2006) were able to stably simulate drops
trapped between solid particles with drop-solid spacing 1% of the particle size, by constructing analytical
expressions to desingularize the single- and double-layer contributions from spherical and spheroidal
particles. Obtaining these closed-form expressions is nontrivial even for simple shapes; for spheroids,
infinite series involving spheroidal harmonics are required. In the case of prolate and oblate spheroids,
these expressions were shown to be fast-convergent. Analytical desingularization of BIM is also successful
for tight drop squeezing through a torus using the tool of toroidal harmonics (Ratcliffe et al., 2010). For
more complex shapes, however, analytical BIM desingularizations are unlikely to be available. Therefore we introduce two methods, one of which is semi-analytical but limited to drop squeezing between axisymmetric shapes (in arbitrary 3D orientations, though), and the second one is general for boundary-integral simulations of drops squeezing between arbitrary Lyapunov surfaces.

The general problem formulation, non-dimensional form and description of particle shapes are provided in §2.2. The boundary-integral equations and additional implementation details are discussed in §2.3. Two distinct methods for high-accuracy calculation of desingularization integrals over various classes of particles are introduced in §2.4. The objective of devising these methods was to overcome a fundamental limitation of the boundary-integral method, namely its numerical breakdown when fluid interfaces closely approach solid surfaces, in cases where analytical or extrapolation techniques are not suitable. Using either of these methods in conjunction with the suite of high-order desingularization techniques outlined by Zinchenko & Davis (2006), generalizes high-accuracy BIM simulations to previously-untenable multiphase systems. One method is semi-analytical and applies to axisymmetric particles. The other, termed the multimesh method, is purely numerical but can accommodate arbitrary smooth shapes. Close agreement is observed between the two desingularization methods, for drop squeezing between cylindrical particles over a range of parameters. The semi-analytical method is considerably faster, and both methods are susceptible of parallelization. To achieve stable simulations over the full range of desired particle shapes, particularly those with high curvature, a coordinated adaptive remeshing scheme for the droplet was also devised, capable of economically maintaining the high resolution of an unstructured mesh within a specific spatial region. In §§2.5-2.6, we report the simulated behavior of drops squeezing between several general classes of particle shapes.

2.2 Definitions of particle shapes and dimensionless numbers

Consider a single freely-suspended drop within a uniform far-field flow, approaching one or more complex-shaped particles fixed in space; Newtonian Stokes flow is assumed inside and outside the drop. The boundary-integral formulation assumes all surfaces have smoothly varying normals. Still, the class of
smooth, closed surfaces is an infinite parameter space; herein we focus on rounded cylinders (capsules) and thin, rounded cuboids (plates), as models for common experimental setups as well as fibrous and other porous media. Several well-defined asymmetric constrictions and particles are also considered (§2.5.4-2.5.5), in order to elicit more complex drop behavior. Hereafter, $N_\triangle$ and $\tilde{N}_\triangle$ will refer to the number of triangles in each solid-particle and drop mesh, respectively. The drop mesh resolution is fixed at $\tilde{N}_\triangle = 11520$ unless noted otherwise, while particle resolution varies greatly depending on size and adaptive resolution. For spheres, capsules and derivative particles, the characteristic length $L$ is a radius of the solid particle (figure 2.1). In the case of rounded plates, $L$ is defined as the gap between two plates forming a constriction. The drop centre is initially placed $10L$ upstream from the particles’ basal plane, unless noted otherwise. The ratio of the drop viscosity ($\mu_d$) and external medium viscosity ($\mu_e$) is $\lambda = \mu_d/\mu_e$, and the uniform far-field velocity carrying the drop towards the constriction is $u_\infty$. The capillary number is defined as

$$Ca = \frac{\mu_e |u_\infty|}{\sigma} \frac{\tilde{a}}{L},$$

(2.1)

where $\tilde{a}$ is the non-deformed drop radius and $\sigma$ is the constant surface tension of the surfactant-free drop interface.

The instantaneous drop velocity $U$, defined as the volume-averaged fluid velocity $u$ inside the drop, can be calculated through the divergence theorem as

$$U = \langle u \rangle = \frac{1}{V} \int_S (u \cdot n)(x - \tilde{x}^c) \, dS,$$

(2.2)

where $V$ is the drop volume, $n$ are outward surface unit normals at points $x$ on the surface, and $\tilde{x}^c$ is the drop centroid. In what follows, $U$ is the component of $U$ along $u_\infty$.

The solid particles used to build constrictions are shown in figure 2.1. A capsule, or spherocylinder, is a round cylinder capped with hemispheres, with a maximum dimension $L$. A range of lengths $L$ are tested; however, a default of $L = 6$ is used for parametric studies. A half-capsule is constructed by dividing a capsule ($L = 6$) in half lengthwise, and capping the resulting sharp edge with a circular bevel of radius...
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Figure 2.1: Particle shapes used to construct constrictions (as well as individual-particle obstacles, in the case of the capsule). The capsule is a cylinder capped with hemispheres on either end. The half-capsule is a capsule cut in half lengthwise, and then capped with a bevel of radius $0.2L$. The flat plate is a simple $4\times 8\times 0.2L$ rectangular prism with beveled edges. Particles not shown to scale.

$0.2L$. As shown below, constrictions are formed by two parallel capsules or half-capsules, separated by a minimum gap of $0.5L$. A plate is a rectangular prism beveled to preserve its original maximal dimensions. In all cases, the plate dimensions are $4\times 8\times 0.2L$, where $L$ is the minimum distance between two plates forming a constriction.

2.3 Desingularized boundary-integral formulation (clean drops)

The present boundary-integral formulation for drops interacting with arbitrary smooth particles utilizes the suite of desingularization methods detailed by Zinchenko & Davis (2006), but replaces all involved analytical desingularization integrals with semi-analytical or numerical integrals. The semi-analytical desingularization for axisymmetric particles and the numerical method for arbitrary surfaces are outlined in §2.4. The Hebecker representation is used for each solid-particle contribution as a linear combination of single-layer and double-layer potentials, and the interfacial stress contribution is desingularized for both drop self-interactions and drop-solid contributions. The resulting Fredholm integral equations of the second kind are well-behaved for tight-squeezing drops, for which drop-solid separation distances can be several orders of magnitude smaller than the system’s characteristic length.

Let $\tilde{N}$ be, for generality, the number of drops in the system, $\tilde{S}$ be the surfaces of these drops, $\hat{N}$ be
the number of solid particles and \( \hat{S} \) be the surfaces of these particles. The no-slip boundary condition \( u = 0 \) is enforced for the fluid velocity on the solid boundaries. The far-field velocity \( u_\infty(y) \) away from the particles and drops can be an arbitrary Stokes flow (although a uniform \( u_\infty \) was assumed in the present simulations). Standard Wielandt’s deflation is used to avoid ill-conditioning at the low viscosity ratios of interest for this study. To this end, the system is cast in terms of \( w = u - \kappa u' \), where \( \kappa = (\lambda - 1)/(\lambda + 1) \) and \( u' \) is the rigid-body projection of \( u \) on a drop surface. At every time step, the following system of equations is solved for modified interface velocity \( w \) on drops and Hebeker density \( q \) on solid surfaces (Zinchenko & Davis, 2006):

\[
\begin{align*}
  w(y) &= \frac{2F(y)}{\lambda + 1} + \kappa \left[ 2 \sum_{\beta=1}^{\hat{N}} \int_{\hat{S}_\beta} w(x) \cdot \tau(r) \cdot n(x) dS_x - w'(y) + \frac{n(y)}{S_{\alpha}} \int_{S_{\alpha}} w \cdot n dS \right] \\
  &+ \frac{2}{\lambda + 1} \sum_{\beta=1}^{\hat{N}} \int_{\hat{S}_\beta} q(x) \cdot [2 \tau(r) \cdot n(x) + \eta G(r)] dS_x \quad (2.3)
\end{align*}
\]

for \( y \in \hat{S}_\alpha \) and

\[
\begin{align*}
  q(y) &= F(y) + (\lambda - 1) \sum_{\beta=1}^{\hat{N}} \int_{\hat{S}_\beta} w(x) \cdot \tau(r) \cdot n(x) dS_x \\
  &+ \sum_{\beta=1}^{\hat{N}} \int_{\hat{S}_\beta} q(x) \cdot [2 \tau(r) \cdot n(x) + \eta G(r)] dS_x \quad (2.4)
\end{align*}
\]

on solid-particle surfaces \( y \in \hat{S}_\alpha \). Here, \( r = x - y \), \( n \) is the unit normal to a surface, \( \eta > 0 \) is the Hebeker parameter (the choice of \( \eta \) affects the algorithm robustness, but not the solution upon numerical convergence), and prime indicates rigid-body projection. The single-layer terms containing the Hebeker parameter \( \eta \) serve to complete the range of boundary-integral operators; without these terms, the double-layer boundary-integral contribution could not accommodate non-zero hydrodynamic forces or torques acting on the solid particles. The inhomogeneous term is

\[
F(y) = u_\infty(y) + \frac{1}{\mu_e} \sum_{\beta=1}^{\hat{N}} \int_{\hat{S}_\beta} 2\sigma(x)k(x)n(x) \cdot G(r) \, dS_x, \quad (2.5)
\]

where \( k \) is the mean surface curvature \( k(x) = (k_1 + k_2)/2 \), with \( k_1, k_2 \) being the principal curvatures at \( x \).
Finally, \( G(r) \) and \( \tau(r) \) are the free-space Green tensor and the corresponding fundamental stresslet, respectively:

\[
G(r) = -\frac{1}{8\pi} \left[ I + \frac{rr}{r^3} \right], \quad \tau(r) = \frac{3}{4\pi} \frac{rrr}{r^3}.
\] (2.6)

After desingularization of droplet-droplet, droplet-particle, and particle-particle interactions, equations (2.3)-(2.4) are solved by GMRES iterations, and the drop node positions are time-integrated using a second-order Runge-Kutta scheme. Mesh quality is maintained using passive mesh stabilization, as in Zinchenko & Davis (2006), and in some cases the customizable remeshing technique described in §2.4.

2.4 Numerical method: obtaining highly-accurate surface integrals

2.4.1 General desingularization formulae

A repository of desingularization techniques that permit stable hydrodynamic interactions between drops and solid particles is provided by Zinchenko & Davis (2006), including drop and solid self-interactions, solid-solid interaction, solid-drop and drop-solid contributions. In certain cases (solid self-interaction, solid-solid interaction, and solid-drop contributions), additional integrals appear during the subtraction procedure that must be calculated with near-analytical accuracy to facilitate tight-squeezing simulations. The complete desingularization expressions and relevant ‘high-accuracy integrals’ in each case are listed below.

For solid-self interaction \((y \in \hat{S}_a)\), singularity subtraction is provided by

\[
\int_{\hat{S}_a} q(x) \cdot [2\tau(r) \cdot n(x) + \eta G(r)] \, dS_x \\
= q(y) + \int_{\hat{S}_a} [q(x) - q(y)] \cdot [2\tau(r) \cdot n(x) + \eta G(r)] \, dS_x + \eta q(y) \int_{\hat{S}_a} G(r) \, dS_x, \quad (2.7)
\]
where the final integral on the right-hand side of (2.7) must be computed with high-accuracy.

Solid-solid interactions are transformed slightly differently, but contain the same integral requiring near-analytical treatment:

\[
\int_{\hat{S}_\beta} q(x) \cdot [2\tau(r) \cdot n(x) + \eta G(r)] \, dS_x
\]

\[
= \int_{\hat{S}_\beta} [q(x) - q(x^*)] \cdot [2\tau(r) \cdot n(x) + \eta G(r)] \, dS_x + \eta q(x^*) \int_{\hat{S}_\beta} G(r) \, dS_x, \tag{2.8}
\]

where \( x^* = x^*(y, \beta) \) is the mesh node on \( \hat{S}_\beta \) closest to \( y \in \hat{S}_\alpha \neq \hat{S}_\beta \).

Likewise, the single-layer part of the solid-drop contribution utilizes a simple regularization also involving \( G(r) \):

\[
\int_{\tilde{S}_\beta} q(x) \cdot G(r) \, dS_x = \int_{\tilde{S}_\beta} [q(x) - q(x^*)] \cdot G(r) \, dS_x + q(x^*) \int_{\tilde{S}_\beta} G(r) \, dS_x. \tag{2.9}
\]

Finally, the high-order near-singularity subtraction used for solid-drop double-layer contribution was found to be especially critical for stable tight-squeezing simulations. To this end, for \( y \) on a drop surface \( \tilde{S}_\alpha \) and its nearest mesh node \( x^* \) on a solid surface \( \hat{S}_\beta \), the density function \( q(x) \) near \( x^* \) is approximated by \( q(x^*) \) plus a linear function \( \mathcal{L}(x - x^*) \); the coefficients of the linear form \( \mathcal{L} \) are found by least-squares fitting to the values of \( \Delta q(x^j) = q(x^j) - q(x^*) \) in the solid mesh nodes \( x^j \) directly connected to \( x^* \).

Subtracting \( q(x^*) + \mathcal{L}(x - x^*) \) from \( q(x) \) completely desingularizes the double-layer part of the solid-drop contribution in (2.3), but gives rise to added-back integrals, which need to be handled either analytically (possible only for a few shapes), or, in general, numerically with high accuracy. This desingularization can be written as
\[
\int_{S_\beta} q(x) \cdot \tau(r) \cdot n(x) \, dS_x =
\int_{S_\beta} [q(x) - q(x^*) - \sum_{j \in A(x^*)} (c_j \cdot (x - x^*)) \Delta q(x^j)] \cdot \tau(r) \cdot n(x) \, dS_x +
\sum_{j \in A(x^*)} [c_j \Delta q(x^j)] \cdot \frac{3}{4\pi} \int_{S_\beta} \frac{r \cdot n(x)}{r^5} \, dS_x,
\tag{2.10}
\]

where \( A(x^*) \) is the set of nodes directly connected to \( x^* \); the vector coefficients \( c_j \) depend only on the local mesh geometry near \( x^* \) and are pre-calculated as detailed in §3 of Zinchenko & Davis (2006).

So, high-accuracy computation of three integral terms is required. Up to a factor, we denote these terms as

\[
G_1(y, \beta) \equiv \int_{S_\beta} \frac{1}{r} \, dS_x, \quad G_2(y, \beta) \equiv \int_{S_\beta} \frac{rrr}{r^5} \, dS_x,
\tag{2.11}
\]
\[
\Psi(y, \beta) \equiv \int_{S_\beta} \frac{(r \cdot n(x)) rrr}{r^5} \, dS_x.
\tag{2.12}
\]

It is advantageous that the second-rank tensor \( G_2 \) and the third-rank tensor \( \Psi \) are fully permutable in their indices, thus reducing the amount of work to calculate these tensors.

2.4.2 Semi-analytical desingularization for axisymmetric particles

Axisymmetric particles permit semi-analytical calculation of the integrals (2.11-2.12), by closed-form azimuthal integration around the particle axis of rotation, with external numerical integration along the particle half-contour. This kind of approach has been widely used in axisymmetric boundary-integral solutions (e.g., Rallison & Acrivos (1978); Lee & Leal (1982); Davis (1999); Ratcliffe et al. (2010)) by reducing the azimuthal integration to elliptic integrals (as discussed in detail by Pozrikidis (1992)). In the present 3D work, analytical azimuthal integration for the high-order subtraction tensor (2.12) is a more cumbersome, but still very efficient approach. As shown in figure 2.2, a representative integration circumference \( C \) is the perimeter of a representative disk of radius \( \rho \), a sufficient number \( \hat{N} \) of which form
an approximation to the axisymmetric volume. The surface integral of a function \( f(x) \) is simply

\[
\int_{S_3} f(x) \, dS_x = \int \rho \, ds \left[ \oint \! C_f(x) \, d\Psi \right],
\]

where \( \Psi \in [-\pi, \pi] \) is the azimuthal angle of rotation around the particle axis, and \( ds \) is the contour length element along the particle’s half-contour.

Now, we outline derivations for closed-form expressions for the integrals (2.11-2.12) over a representative circumference \( C \), in terms of complete elliptic integrals of the first and second kind. Let the origin \( O \) of the temporary coordinate system \((\rho \cos \psi, \rho \sin \psi, z)\) be at the centre of \( C \), with its axis of revolution along the z-axis (figure 2.2). Without loss of generality, the x-axis can be defined as antiparallel to the shortest vector from the z-axis to the observation point \( x_0 \). The observation point is then \( x_0 = (-\rho_0, 0, z_0) \) and the vector \( r = x - x_0 \) between \( x_0 \) and a integration point \( x \) on \( C \) is given by

\[
r = (\rho \cos \psi + \rho_0, \rho \sin \psi, z - z_0),
\]

and

\[
r^2 = \left[ (\rho + \rho_0)^2 + (z - z_0)^2 \right] \left[ 1 - k^2 \sin^2 \frac{\psi}{2} \right], \quad \text{where } k^2 = \frac{4\rho \rho_0}{(\rho + \rho_0)^2 + (z - z_0)^2}.
\]

The simplest contour integral over \( C \) relevant to computing \( G_1 \) may be expressed as

\[
\int_{-\pi}^{\pi} \frac{1}{r} \, d\psi = c_0 \int_{-\pi}^{\pi} \left[ 1 - k^2 \sin^2 \frac{\psi}{2} \right]^{-1/2} \, d\psi = 4c_0 F.
\]

where \( c_0 = ((\rho + \rho_0)^2 + (z - z_0)^2)^{-1/2} \) and \( F \) is the complete elliptic integral of the first kind with modulus \( k \). The relevant integrals over \( C \) for \( G_2 \) and \( \Psi \) can be derived in a similar manner and final expressions are provided in appendix 2.A. Once \( G_2 \) and \( \Psi \) are computed in the special coordinate basis defined above, they are then transformed by usual tensor transformation rules to the global basis used in the squeezing simulation.
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Figure 2.2: An axisymmetric particle oriented as a surface of revolution $\tilde{S}_\beta$ around the z-axis. The single- and double-layer contributions of circular segments can be calculated analytically using elliptic integrals. For a given representative circle $C$, the origin $O$ may be placed at its center, with the x-axis in plane but oriented away from the observation point $x_0$. Cylindrical coordinates $(\rho, \psi, z)$ are used for deriving elliptic integral calculations.

The present semi-analytical approach results in very fast and accurate calculation of single- and double-layer desingularization integrals (2.11) and (2.12) for axisymmetric particles. Surface integrals calculated by (2.13) converge quickly with respect to $\tilde{N}$ (with second-order Euler external integration). For example, using a capsule ($L = 6$) as a test particle and an observation point $0.01L$ away from the cylindrical section of particle surface, all $\Psi$ terms agree to within at least the fifth decimal point for $\tilde{N}$ values of 1000 and 10000. The former corresponds to a representative disk width of 0.006. Further convergence tests and comparisons with the multimesh method are provided in §2.5.1.

2.4.3 Multimesh desingularization

Desingularization for arbitrarily-shaped particles can be achieved with direct numerical calculation of $G_1$, $G_2$ and $\Psi$ (2.11-2.12), if sufficiently-high resolution meshes are used to discretize these surface integrals. Note that this ‘multimesh desingularization method’ still requires particles to have smoothly varying normals (i.e. to be Lyapunov surfaces). Extremely high resolutions are required for single- and double-layer contributions to approach exact values, in order to accurately and stably reproduce analytical or semi-analytical tight-squeezing results. Due to the singular nature of the integrals, accuracy is more sensitive to mesh resolution as the observation point approaches the particle surface; therefore, a hierarchy of embedded meshes is used for multimesh desingularization.

Two high-resolution auxiliary meshes are used for desingularization integrals. The first high-resolution mesh typically has four times more triangles than the basic mesh used for BIM calculations.
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The second is an ultra-high-resolution mesh, typically 64 times denser than the basic mesh, as shown in figure 2.3a-b. For particles with higher surface area, the ultra-high-resolution mesh may have in excess of 2.5 million triangles. Therefore, the two meshes are chained to each other: the 16 ultra-high-resolution triangles within each high-resolution triangle are pre-calculated and stored. In contrast to BIM calculations for desingularized terms, the desingularization surface integrals for multimesh calculations are discretized in terms of triangles, not nodes. If the distance between a given observation point \( x_0 \) and the centroid of a high-resolution triangle is greater than a prescribed distance cutoff \( r_c \), then that distance and corresponding triangle area are used as an area element. Otherwise, the 16 corresponding higher-resolution triangles are substituted during evaluation of the integral terms. The desingularization integrals for solid self-interaction and solid-solid interactions are calculated only once at the start of each simulation, so a high distance cutoff \( (r_c = 1.0L) \) was used with a negligible penalty on total CPU time. The solid-drop contribution to the desingularization integrals is computed outside of GMRES iterations, but still represents the slowest operation of the multimesh method. A distance cutoff of \( r_c = 0.4L \) for the solid-drop contribution was found sufficient to stably model tight-squeezing or trapped drops with accuracy approaching that of analytical methods, as discussed in §2.5.1.

Several technical issues arise due to the requirements of 1) quality meshing of arbitrary shapes, 2) sufficient precision for node positions and normals, 3) memory requirements of ultra-high-resolution meshes and 4) mesh chaining. An approximate mesh for each particle resolution was created using the powerful open-source software Blender, which has no limitation on mesh size and can easily handle meshes with \( N_\Delta > 2.5 \) M, but uses single-precision floating-point format for coordinates. After node positions and connectivity are exported from Blender, coordinates are read into the BIM program and adjusted to double-precision according to piecewise analytical functions that define a given particle shape. Due to memory considerations, only one instance of each desingularization mesh is saved in memory, and is translated and/or mirrored (see §2.4.4) during calculations over a given particle. Finally, an efficient algorithm was written to chain two meshes to each other, based only on node positions and connectivity, and assuming every high-resolution node coincides with an ultra-high-resolution node. Briefly, coinciding nodes between the meshes are determined by position, and a nearby ultra-high-resolution triangle is
Figure 2.3: Solid-particle meshes used for the $L = 4$ capsule by the multimesh desingularization method. (a) The high-resolution ($\tilde{N}_\Delta = 52$ K) and ultra-high-resolution ($\tilde{N}_\Delta = 840$ K) meshes used for numerical desingularization. The additional edges of the ultra-high-resolution mesh are colored cyan. (b) The basic mesh ($\tilde{N}_\Delta = 13$ K) used by the BIM simulation for desingularized terms. (c) A given observation point $x_0$ calculates per-triangle values from the ultra-high-resolution mesh within a cutoff $r_c$.

associated with a given high-resolution triangle if its centroid (projected along the surface normal) lies within the perimeter of the high-resolution triangle.

2.4.4 Additional numerical considerations

Two configurations, drop flow around a single capsule and between two flat plates, presented particular challenges regarding numerical stability and drop mesh quality. A useful extension of the commonly-used triangle subdivision scheme introduced by Cristini et al. (2001) was developed, which is particularly effective when remeshing contiguous regions on a drop. The simple idea is, given a list of all triangles to be subdivided within a given region, a uniform mesh four times denser than the original can immediately result, by adding nodes at all edge midpoints and appropriately connecting them (see appendix 2.B).
Connectivity around the perimeter of this region can also be determined simply, e.g. in the manner of Cristini et al. (2001) (§A.1.2. therein). Occasional node addition on regions of contiguous triangles had two benefits. First, a much cleaner mesh immediately resulted, such that further relaxation tangential to the drop surface was unneeded. Second, updating the mesh topology was required much less often, resulting in a more efficient algorithm. For example, in the case of a single drop approaching a single fiber, passive mesh stabilization alone (in the form of Zinchenko & Davis (2006)) was found to be inadequate due to the massive drop deformation. This simulation was greatly extended by defining an upper limit on triangle area, and whenever this limit was reached, executing node addition on all triangles within a cutoff distance of the triangle with maximal area. In this case, similar simulation times were reached by actively redistributing nodes using an advanced potential energy function (Zinchenko & Davis, 2013). A paraboloid fitting of surrounding nodes’ positions was used to choose coordinates for the inserted nodes. Including the second- and third-level neighbors in the fit greatly improved the local curvatures at inserted nodes, in areas of both low and high curvature. Note that a four-times-denser triangle mesh corresponds to mesh edges one half their original length; the tighter Courant stability limitation on the time step was not prohibitive for any systems presented herein. To maintain mesh quality on the whole drop, passive mesh stabilization (Zinchenko & Davis, 2006) is also enforced for all nodes at every time step.

The above ‘coordinated adaptive remeshing’ scheme was extended to allow added nodes to be subsequently removed. In the case of a drop squeezing between thin plates, especially at low capillary numbers, it was necessary to include a spatially-dependent remeshing scheme for the drop surface, with criteria defined to increase mesh resolution within near-contact regions of the drop (figure 2.4a–b). In this case, the drop does not experience particularly high deformation or curvatures, yet mesh stability greatly benefits from increased resolution in specific regions. This criteria-based local remeshing is achieved by remembering the original mesh connectivity, restoring it and re-evaluating the given criteria for refinement (every so many time steps). Therefore, the region of higher mesh resolution shown in figure 2.4 remains constant as the drop moves through the constriction. This technique was also necessary for certain half-capsule configurations at low capillary number.

To prevent symmetry breaking during drop flow, it was necessary that individual solid-particle
Figure 2.4: Adaptive mesh schemes for droplet squeezing between plates. (a) Coordinated adaptive meshing of drop surface based on spatial criteria. By storing the original mesh connectivity and reevaluating the criteria before every remeshing, the region of denser triangulation remains constant as the drop moves through the constriction. (b) Orthogonal view of the same drop, with solid particles hidden.

meshes were made symmetric with respect to all three orthogonal planes that pass through the constriction centre. Also, for the flat-plate system, a fixed adaptive mesh was used for solid particles to increase node density in near-contact regions. Mesh density within two unit lengths of the constriction centre was increased between four and sixteen times, depending on proximity to the constriction centre. This base mesh was refined to create the higher-resolution desingularization meshes. In order to maintain the aforementioned symmetry, while also storing only one copy of the higher-resolution meshes in memory, a value is associated with each particle to indicate whether or not to use the mirror image of a given mesh. Inverting a coordinate is not computationally intensive, allowing for symmetric systems with nonuniform meshes to be efficiently treated within the framework of the multimesh desingularization method.
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2.5 Drops squeezing between complex shapes: numerical simulations

All values from the numerical simulations of drop tight squeezing are reported in non-dimensional form. The characteristic length scale \( L \) is taken as the solid-particle radius \( \hat{a} \) for capsules and derivative particles; for plates, \( L \) is the gap between two particles. The velocity and times scales are \( |\mathbf{u}_\infty| \) and \( L/|\mathbf{u}_\infty| \), respectively. The Hebeker parameter \( \eta \) in the boundary-integral formulation (equations 2.4-2.3) is set to unity. The initial drop shape is spherical and far upstream from the constriction. The definitions of \( \text{Ca} \) and \( \lambda \) are provided in §2.2. For brevity, the abbreviations 5 K, 8.6 K and 11.5 K will be used for \( \hat{N}_\Delta = 5120, 8640, 11520 \). Higher solid-particle resolutions, whose nodes are typically not uniformly distributed, will be similarly rounded. Unless noted otherwise, the droplet resolution is 11520 (\( \hat{N}_\Delta = 11.5 \text{ K} \)). Three meshes are used for each solid particle in the multimesh desingularization method. Their triangle counts are reported as a multiple of the basic mesh resolution. For example, if the high-resolution mesh is four times denser than the basic mesh, and the ultra-high-resolution is 16 times denser than the high-resolution mesh, all three triangle counts are reported as \( \hat{N}_\Delta = 8.6 \text{ K} \times 4 \times 16 \).

2.5.1 Convergence with mesh resolution and desingularization methods

Convergence of results for the default capsule length (\( \mathcal{L} = 6 \)) with respect to solid-particle mesh resolution is shown in figure 2.5. The \( \hat{N}_\Delta = 35.6 \text{ K} \) mesh utilized adaptive resolution such that the mesh was four times denser within a distance of \( \approx 1.4 \) from the constriction centre, compared to the \( \hat{N}_\Delta = 20.2 \text{ K} \) mesh. Although \( \hat{N} = 1500 \) was set throughout this work for the number of characteristic disks used in the semi-analytical method (increased for longer capsules to provide an equivalent linear density), figure 2.5 also shows that half that number produces reasonable results (resulting in an eight-times speedup for desingularization as compared to the multimesh method). Our multimesh implementation was validated against previous results that used analytical desingularization (Zinchenko & Davis, 2006), and the multimesh and semi-analytical methods were compared against each other. As shown in figure 2.6, good agreement is seen for drops squeezing between spheres and spheroidal particles. These two-particle
Figure 2.5: Convergence of the drop velocity for squeezing between two capsules (\(\mathcal{L} = 6\)) with respect to solid-particle mesh resolution \(\hat{N}_\Delta\) and number of characteristic disks \(\hat{N}\) used for semi-analytical desingularization (\(\lambda = 4.0, \tilde{a} = 0.5, \epsilon = 0.5\)).

Constrictions, especially the spheroidal system, are prone to symmetry breaking and sensitive to mesh resolutions, so reproducing these tight-squeezing results efficiently and without analytical expressions was unexpected. In addition to global accuracy, the multimesh method was necessary to maintain a smooth drop mesh in near contact regions. For these tests, each higher-resolution mesh was 16 times denser than the previous mesh in the hierarchy. Further increasing these desingularization-mesh densities negatively impacted performance while negligibly affecting droplet dynamics. As shown in figure 2.6, close agreement was also observed between the multimesh and semi-analytical desingularization techniques for drop squeezing between axisymmetric particles, even for tight squeezing.

### 2.5.2 Single capsule

Capsules are presented as a prototype for fibrous material. First, consider a drop approaching a single capsule (\(\mathcal{L} = 6\)). Patel et al. (2003) introduced this configuration experimentally, and provided boundary-integral results for a drop approaching an infinitely long cylinder. Patel et al. avoided the Stokes
Figure 2.6: Comparison between two types of desingularization methods ($\tilde{N}_\Delta = 8.6$ K, $\hat{N}_\Delta = 5$ K $\times 16 \times 16$). Insets shows snapshot of simulation at $U_{\text{min}}$. (a) Multimesh and analytical desingularization methods agree well for drop squeezing between two spheres ($\epsilon = 0.5, \tilde{a} = 0.9, Ca = 0.63, \lambda = 4.0$). (b) Drop squeezing between two parallel oblate spheroids with major and minor axes of 1 and 0.4, respectively ($\epsilon = 0.5, \tilde{a} = 0.75, Ca = 0.4, \lambda = 1.0$).
paradox by using a disturbance field based on the Brinkman equation for an isotropic porous medium, and assuming the drop does not hydrodynamically interact with the fiber. In the present case, the full hydrodynamic effects, including lubrication, are included in accordance with the Stokes equation, for which a solution is possible because the capsule is of finite length. The effect of particle length is discussed in more detail in the context of the two-capsule constriction.

Patel et al. (2003) identified two modes of drop breakup: a grazing mechanism in which drop breakup occurs downstream from the fiber, and hairpin formation when the drop passes around either side, resulting in two bulbous ends, or lobes, connected by a thin filament. The mode of breakup primarily depends on the initial horizontal offset $\epsilon$ of the drop from the center of the capsule. In all cases for the present single-capsule study, system parameters are $Ca = 3.0, \lambda = 1.0, \text{ and } \bar{a} = 1.5$, which are typical values used by Patel et al. (2003), and the drop is initially placed 10$L$ upstream from the capsule. Hairpin formation was observed for $\epsilon \leq 0.6$, the grazing breakup mechanism was observed for $\epsilon = 0.7$ and the drop remains stable (separation without breakup) for $\epsilon \geq 0.75$. The drop velocity $U$ corresponding to various mechanisms is shown vs. time in figure 2.7a. Despite the apparent similarity between $\epsilon = 0$ and $\epsilon = 0.1$, overall drop behavior is highly sensitive to the initial offset. For example, for an offset of $\epsilon = 0.1$, 59% of the drop (by volume) passes around one side of the capsule. Typical configurations during hairpin formation are shown in figure 2.7b. As discussed further below, a large gap ($\approx 0.2$) remains between the filament and the solid particle, while the majority of drop has passed downstream. The drop diameter, defined as the maximum distance between any points on the drop and normalized by drop radius, is shown in figure 2.7d, highlighting the system’s sensitivity to initial drop offset.

The lubrication layer between the filament and the fiber influences the drop-particle gap, and this layer is affected by the shape of the filament. This effect is demonstrated using a drop offset of $\epsilon = 0.3$ as shown in figure 2.8a, which results in a drop shape resembling those observed experimentally by Patel et al. (2003) (see figure 4 therein). As the filament initially nears the particle face, it spreads axially and an elongated dimple forms along the transverse direction. During this phase, the gap plateaus with respect to time, before decreasing abruptly as the filament thins. This decrease in separation corresponds to the flattening of the dimple into a convex filament. Cross sections of the filament directly above the capsule
Figure 2.7: Droplet flow around a single capsule ($Ca = 3.0, \lambda = 1.0, \bar{a} = 1.5, L = 6.0$). (a) Volume-averaged drop velocity vs. time as a function of drop offset. The drop remains stable for $\epsilon \geq 0.75$. (b) Typical configurations during the hairpin breakup mechanism. (c) Drop-particle gap as a function of time and drop offset. (d) Drop diameter is sensitive to offset. Length is the maximum distance between any two points on the drop normalized by the undeformed drop radius (curves for $\epsilon = 0.6$ and 0.7 are very similar to $\epsilon = 0.5$).
Figure 2.8: Droplet undergoing massive deformation around a capsule ($Ca = 3.0$, $\lambda = 1.0$, $\tilde{a} = 1.5$, $L = 6.0$) (a) Droplet approaching breakup via the hairpin mechanism. (b) Rate of lubrication layer thinning correlates with the cross-sectional shape of the filament (cross-sectional plane indicated by gray line in frame (a)).

centre are shown as insets in figure 2.8b. The dimple formation shown at $t = 30$ is dependent on the capsule length; for example, using a capsule of length $L = 10$, the filament remains less concave at it approaches the cylindrical surface.

### 2.5.3 Two-capsule constriction

Consider a drop approaching two parallel capsules separated by a gap $\epsilon = 0.5$, where the non-deformed drop diameter is twice the gap and half the solid particle diameter. In contrast to drop interactions with a single capsule in unconfined flow, the drop tends to remain compact throughout the squeezing process. An important binary property of this system is whether or not the drop will pass through the constriction; as shown in figure 2.9a, the drop is trapped below a critical capillary number. There is excellent agreement between the multimesh ($\hat{N}_\Delta = 20.2$ $K \times 4 \times 16$) and semi-analytical ($\hat{N} = 1500$) methods, while the semi-analytical calculations were four to eight times faster. As observed for drops squeezing between spheres, the minimum drop-particle gap is almost insensitive to $Ca$ (figure 2.9b), although this separation
remains slightly larger compared to drop squeezing through a three-sphere constriction (Zinchenko & Davis, 2006). The tendency of the trailing end of the drop to approach the solid surface more closely as it is exiting, as compared to the majority of the squeezing process (gap decrease ≈ 30%), is more pronounced for capsules than, e.g., drop squeezing between three spheres. Presumably, the differing nature of the lubrication layers is responsible for this effect; as discussed in §2.5.5, the effect is even more pronounced for drops squeezing between flat plates. A snapshot of a supercritical drop when it is approximately centred in the constriction is shown in figure 2.9c. The drop profile at the centre of the constriction is outlined by the dashed line in the inset. This dimple in the drop surface is less pronounced during the early and late stages of squeezing. A steady-state trapped drop is also shown from axial and transverse perspectives (figure 2.9d). The transverse drop profile is approximately circular, as is the case for supercritical drops at a similar position.

Drop squeezing is significantly affected by capsule length, even for long capsules with ends far from the drop. For example, repeating the two-sphere simulation above (ϵ = 0.5, ˜a = 0.9, Ca = 0.63, λ = 4.0), but replacing the spheres with capsules of length L = 4, results in vastly different behavior. As shown in figure 2.10a, the minimum drop velocity \( U_{\text{min}} \) is 5% of far-field velocity for the two-sphere constriction, whereas the drop becomes trapped in the two-capsule constriction. A parametric study of the effect of cylinder length on droplet trapping was completed at \( Ca = 1.5, \lambda = 4.0, ˜a = 0.5 \) and \( \epsilon = 0.5 \). One might expect drop velocities to converge relatively quickly after the capsules reach a certain length, due to the diminishing end effects. However, a notable difference in drop velocities and squeezing times was observed between L values of 4, 6, 8 and 10, as seen in figure 2.10b. This disparity was not significantly alleviated by rescaling the capillary number individually for each system, based on the flow velocity at the centre of the constriction (in an attempt to minimize the effect of the far-field flow \( u_{\infty} \)). The lack of convergence is attributed to variations in the undisturbed (single-phase) flow and can be directly related to the size-effect problems that plague both experimental and numerical studies of the Stokes paradox for flow past long cylinders. For example, Khalili & Liu (2017) demonstrate that, for 3D cylinders, immense aspect ratios are required for convergence of results as Reynolds number goes to zero. Furthermore, velocity fields do not converge with decreasing Reynolds number (although unintuitive, this lack of convergence is less surprising
Figure 2.9: Droplet squeezing between two capsules ($\lambda = 4.0$, $\tilde{a} = 0.5$, $\epsilon = 0.5$, $L = 6.0$). (a) Droplet becomes trapped below a critical capillary number. An agreement is observed between semi-analytical and multimesh methods ($\bar{N}_\Delta = 20.2 K \times 4 \times 16$). (b) The minimum drop-particle gap is very small for tight-squeezing simulations, and not sensitive to $Ca$. (c) Snapshot as drop passes through a two-capsule constriction above $Ca_{\text{crit}}$. Dashed line in inset outlines drop profile at constriction centre. Two orthogonal views shown. (d) Steady-state drop trapped between two capsules.
Figure 2.10: Effect of capsule aspect ratio on drop squeezing. (a) Cylindrical particles, even at small aspect ratios ($L = 4$), significantly enhance drop trapping ($Ca = 0.63$, $\lambda = 4.0$, $\bar{a} = 0.9$, $\epsilon = 0.5$). (b) Drop trajectories do not converge with respect to capsule length, $L = 4$ to 10 ($Ca = 1.5$, $\lambda = 4.0$, $\bar{a} = 0.5$).

given there is no solution for unbounded Stokes flow around an infinite cylinder). Indeed, the aspect ratios of cylinders tractable for this study are orders of magnitude smaller than Khalili & Liu’s recommendations for converging velocity and pressure fields. A related work is that of Smith (1990) on the Jeffery paradox (an unintuitive result that involves two cylinders in two-dimensions, at least one of which is rotating).

Smith came to a similar conclusion that, when attempting to approach this 2D result using finite 3D cylinders, cylinder aspect ratios must be many-orders-of-magnitude before end effects become negligible. However, it is not the objective of this work to approximate drop squeezing between infinite cylinders, but rather to model a local environment within fibrous material. The default $L = 6$ was chosen as a compromise between capsule length and simulation speed.

Drop behavior is also dependent on viscosity ratio $\lambda$ and non-deformed droplet radius $\bar{a}$. A parametric study of $\lambda$ at $Ca = 1.5$ is shown in figure 2.11a. At low $\lambda$ and high $Ca$, the drop undergoes greater variation in velocity during the squeezing process, and the overall trajectory is more symmetric with respect to time (including the appearance of two global minima for $U$). Although squeezing times increase with $\lambda$, there is no indication of switching from droplet pass-through to trapping within reasonable
As observed for the three-sphere constriction (Zinchenko & Davis, 2006), the drop-particle gap is sensitive to $\lambda$, decreasing from about 0.021 for $\lambda = 10$, to 0.015 for $\lambda = 0.25$. Drop velocity as a function of $Ca$ at low viscosity ratio ($\lambda = 0.25$) is shown in figure 2.11b (for comparison at $\lambda = 4.0$, see figure 2.9a). Parametric studies for $Ca$ also were completed at $\lambda = 1.0$ and 10; in all cases, the viscosity ratio was not observed to alter pass-through vs. trapping, as has been noted for drop squeezing between spheres (Zinchenko & Davis, 2006). Drop size, in contrast, notably affects $Ca_{crit}$. Increasing the drop radius by 50% results in $Ca = 1.5$ being subcritical (figure 2.11c). For $\tilde{\alpha}/\epsilon = 2.0$, where the drop diameter is four times the gap diameter, the drop must undergo massive deformation to pass through. A steady-state trapped drop is shown in figure 2.11d. For this drop size, our simulations indicated pass-through at $Ca = 3$. At $Ca = 4$, the drop flows around the capsules rather than through the constriction (similar to the head-on approach of a drop toward a single capsule, discussed above).

### 2.5.4 Half-capsule constriction

To demonstrate the ability of the multimesh desingularization method to handle more complex geometries and new related physical phenomena, consider a capsule that is cut in half lengthwise with rounded edges (as described in §2.2). Now, the upstream single-phase flow field depends on the particle orientation, as the particles are no longer symmetric with respect to the constriction’s basal plane. Therefore, droplet shape and velocity also depend on the particle orientation (or equivalently, the direction from which the drop approaches the constriction). This dependence is shown in figure 2.12a, where ‘upper half-capsule’ refers to a capsule whose volume in the upper half-space has been retained. For the supercritical case $Ca = 1.5$, a slight but notable difference in $U_{min}$ and squeezing times is observed ($\approx 33\%$ decrease in $U_{min}$). For the subcritical $Ca = 0.9$, particle orientation manifests as a disparity in droplet deceleration as it approaches the constriction (figure 2.12a). The drops have very different shapes at analogous stages of the squeezing process. For example, the drops are compared in figure 2.12c for each orientation at their respective $U_{min}$. These configurations correspond to different lubrication behavior. At their respective $U_{min}$, the drop-particle gap for the lower half-capsule is $\approx 40\%$ lower than the upper half-capsule (similar to the subcritical $Ca = 0.9$ case), and the trajectory-minimum gap disparity is a $\approx 20\%$ (2.12b). While there still
Figure 2.11: Drop squeezing behavior with respect to various system parameters ($L = 6$). (a) Drop velocity is more symmetric with respect to time at lower viscosity ratio $\lambda$ and high $Ca$ ($Ca = 1.5, \bar{a}/\epsilon = 1.0$). (b) Effect of $Ca$ at low $\lambda = 0.25$; $Ca_{\text{crit}}$ is not sensitive to $\lambda$, e.g. compared to $\lambda = 4.0$ (figure 2.9a). (c) Tendency for drop trapping increases with droplet radius ($Ca = 1.5, \lambda = 4.0$). (d) Typical trapped state for a droplet radius of twice the gap diameter ($Ca = 2.0, U = 1 \times 10^{-4}$).
Figure 2.12: Drop squeezing between two half-capsules ($\lambda = 4.0$, $\tilde{a} = 0.6$, $\epsilon = 0.5$, $L = 6$, $\tilde{N}_\Delta = 32.8 \text{ K} \times 4 \times 16$). (a) Drop velocity is sensitive to particle orientation (or equivalently, direction of droplet approach). The disparity between minimum velocity $U_{\text{min}}$ and squeezing times ($Ca = 1.5$) indicates weak flow rectifying behavior. (b) Minimum drop-particle gap as a function of time and particle orientation. (c) Snapshots of each drop at their respective global minimum velocities with respect to particle orientation. (d) The interfacial velocity fields of the drops pictured in (c), from a transverse view.
Figure 2.13: Drop squeezing between two rounded plates ($\lambda = 4.0$, $\tilde{a} = 0.75$, $\epsilon = 1.0$, $\tilde{N}_\Delta = 45.7$ K $\times 4 \times 16$).

(a) Supercritical drop velocity vs time for squeezing between flat plates is notably different than those for more rounded shapes. (b) Drops closely approach rounded flat plates, especially while the drop is exiting the constriction, or for subcritical $Ca$. (c) Evolution of drop shape during the tight-squeezing process ($Ca = 0.9$).

occurs the characteristic dimple formation near the high-curvature edges of the lower half-capsule, the surface area of this region is smaller than for the upper half-capsule case. This finding affects the interfacial velocity field, as shown in figure 2.12d. As compared to a drop in near-contact with a sphere, the surface-divergent flow near the centre of the near-contact region is elongated in the axial direction.

### 2.5.5 Two-plate constriction

Multiphase flow past fixed surfaces with high curvature presents particular numerical challenges for boundary-integral methods. In this case, the undeformed drop has radius $\tilde{a} = 0.75$ and the rounded edge of the plate has a radius of 0.2, representing a curvature ratio of 3.75 (where the characteristic length $L$ is the
gap $\epsilon = 1$ between plates). Note that our algorithm requires smooth versus sharp edges, and that a sharp edge would lead to physical contact due to reduced lubrication. We did not explore the effect of the rounding radius. As described is §2.2, the major plate dimensions are $4 \times 8$, and the constriction is formed by placing two plates on a plane with the gap $\epsilon$ defined as the minimum distance between their longest sides. This configuration has a lower $Ca_{\text{crit}}$ than the systems above, despite the lower drop-radius-to-gap ratio. As shown in figure 2.13a, $Ca = 0.9$ is supercritical and has a similar $U_{\text{min}}$ and squeezing time as $Ca = 1.5$. The drop also passed through the constriction with capillary numbers of 0.7 and 0.5, but reached subcritical behavior with $Ca = 0.3$. The features described in §2.4.4 are collectively able to demonstrate drop trapping in this constriction to sufficiently low velocities, though the simulation was not stable indefinitely; eventually the drop mesh started to overlap with the solid particle. The ability of the multimesh method to model this challenging system efficiently, without code parallelization, is promising, especially considering the extreme approach of the drop interface to the solid particle surfaces. As shown in figure 2.13b, the trailing end of the drop approaches the particle to within $\approx 0.006$ when exiting the constriction, similar to the steady-state separation of the trapped drop. This contrasts with the two-capsule system above, where the minimum gap is $\approx 0.02$, i.e., a decrease of $\approx 70\%$. Snapshots during the squeezing process are shown in figure 2.13c, including the close approach at points of high drop curvature while exiting the constriction. Close inspection of the drop at $t = 150$ also shows a profile with sharp angles in the near-contact region. This profile is not a mesh effect (the coordinated adaptive meshing scheme ensures high drop mesh resolution in this region at all times), but rather is due to the elongated dimple in the drop interface, which approaches the solid particle most closely along its perimeter. The evolution of these drops, suspended in far-field flow and squeezing between rectangular plates, is visually similar from this axial perspective to those of buoyant drops squeezing through circular orifices, see, e.g., Bordoloi & Longmire (2014) and Ratcliffe et al. (2012).

Finally, consider a drop approaching two plates that are angled 45 degrees with respect to the far-field flow. The objective of this configuration was to emphasize the slight drop-rectifying flow displayed by the half-capsule system, perhaps to the extent of demonstrating drop pass-through when approaching from one direction, and trapping or breakup from the other. However, for $Ca = 0.9 - 1.5$, stable
Figure 2.14: Drop squeezing between two plates angled at 45 degrees with respect to the far-field flow ($Ca = 3.0$, $\lambda = 4.0$, $\bar{a} = 0.75$, $\epsilon = 1.0$, $\tilde{N}_\Delta = 45.7$ K $\times$ $4 \times$ $16$). (a) Drop flows stably between downward-angled plates. The X mark indicates simulation exit before imminent drop breakup in the case of plates angled upward. (b) Snapshot of supercritical drop when approximately centred in the downward angled-plate constriction. (c) Mechanism of drop breakup in the case of a drop squeezing between upward-angled plates ($Ca = 3.0$).
supercritical behavior is observed with either plate orientation, and furthermore $U_{min}$ is not sensitive to orientation. At $Ca = 2.0$, the global velocity minimum is lower for upward-angled plates (each plate rotated such that its edge near the constriction centre is moved upstream). A similar disparity is observed at $Ca = 3.0$, as shown in figure 2.14a. However, in this case, while the drop passes stably through the downward-angled plates (figure 2.14b), it will break when flowing through the upward plates. The mechanism for this breakup is shown in figure 2.14c, suggesting the majority of drop volume passes through the constriction, while two significantly smaller drops will flow around the outer faces of each plate.

2.6 Remarks on using BIM for multi-phase flow in complex environments

The multimesh method for simulating tight-squeezing deformable drops between arbitrary Lyapunov surfaces and a semi-analytical formulation using elliptic integrals for axisymmetric particles in a 3D setting were introduced, for use by high-resolution three-dimensional boundary-integral simulations. The semi-analytical formulation was achieved by closed-form azimuthal integrations for single- and double-layer desingularization tensors in terms of complete elliptic integrals of the first and second kind. The total contribution of an axisymmetric particle to a desingularization tensor can then be obtained by integrating the azimuthal contribution along the particle axis. This method was used to simulate tight-squeezing drops between spherocylinders, or capsules, and results agreed well with the multimesh desingularization method.

The multimesh method replaces analytical desingularization integrals with numerically-calculated ones, using a hierarchy of embedded meshes. Two meshes (in addition to the basic mesh) with increasingly higher resolutions were used for desingularization calculations, with the highest resolution typically containing in excess of one million triangles. Memory requirements were kept low by using a template of each high-resolution mesh to represent a given particle by a translation and/or mirror symmetry. These fully three-dimensional simulations remain computationally feasible by using adaptive resolution and mesh chaining techniques, and due to the limited need to recalculate desingularization integrals (outside of GMRES iterations). For the particularly challenging case of drops interacting with high-curvature surfaces,
a coordinated adaptive remeshing scheme for the droplet was introduced. Using these methods, the behavior of drops interacting with a variety of particle types representative of fibers as well as non-axisymmetric shapes was probed over a range of fluid, droplet and particle parameters.

Droplet motion between and around high-aspect-ratio capsules is representative of the commonly-encountered class of multiphase flow through fibrous media. In accordance with the known lack of convergence of Stokes flow with respect to increase of a cylindrical object’s length, drop squeezing behavior was shown to be highly dependent on capsule lengths within the reach of feasible computing. Therefore, a length of $L = 6$ was chosen as the default capsule, such that a wide range of parametric studies could be completed with either the semi-analytical or multimesh method (the axisymmetric method was typically four to eight times faster for this system). The approach of a droplet toward a single capsule was simulated while accounting for all hydrodynamic effects, including lubrication. Several modes of drop breakup were demonstrated, as was the critical drop offset from the capsule centre to incur breakup. During the hairpin mechanism of breakup, a thin filament forms around the capsule after the majority of drop volume has been swept downstream. This filament takes on a concave shape and lubrication forces maintain a large gap between this filament and the solid particle surface; after the filament thins to a convex near-circular cross-section, a sharp decrease in the filament-surface separation occurs. For drop squeezing between two particles, very different behavior and a significant increase in $Ca_{crit}$ are observed between spheres and capsules (even of low aspect ratio). Typical squeezing behavior and shapes for both super- and subcritical drops between capsules were found, including the persistence of dimples in the near-contact region. Drops with radii up to four times the inter-capsule gap were modeled, and stable simulations were possible for both trapping and pass-through at high capillary numbers.

Successful simulations of near-critical drop flow between substantially more arbitrary shapes, including those with high-curvature, was demonstrated with half-capsules (capsules cut in half lengthwise) and thin plates with rounded edges. The challenging case of drop flow between plates with a beveled-edge radii 3.75 times smaller than the undeformed drop radius was handled, including the subcritical $Ca = 0.3$. The minimum drop-particle gap is notably smaller than for more rounded particles with similar system parameters, indicating significantly different lubrication behavior. The half-capsule is not symmetric with
respect to the basal plane of the constriction, and the behavior of drops depends on the particles’ orientation. A drop’s global minimum velocity $U_{\text{min}}$ is lower when it is approaching the flat face of the half-capsule, indicating a slight drop rectifying flow, due to drop interaction with the differing upstream single-phase flow fields. An asymmetric constriction can also be constructed by angling two plates with respect to the far-field flow, creating a finite-size approximation of wedge flow. Despite the significantly-different upstream single-phase flow fields between plate orientations, drops do not exhibit rectifying behavior at moderately-supercritical $Ca$ (as determined by $U_{\text{min}}$). However, at sufficiently high $Ca$, a drop will stably pass between two plates angled downward, but experience breakup while squeezing between upward-angled plates.

High-accuracy simulations of multiphase Stokes flow through arbitrary environments have applications in many fields. The tools developed herein were designed to allow for high-throughput testing of custom particle shapes. Perhaps the most conspicuous way to extend these methods is to scale up to emulsions flowing through many close-packed complex particles, such as cylindrical pellets. Many of the challenges associated with such a simulation have been addressed by Zinchenko & Davis (2013) for emulsion flow through random arrays of spheres. The multimesh method is not anticipated to scale well on a single processor to very large systems. However, poor single-processor scaling may be offset by the fact that the required calculations are both ‘perfectly parallel’ and easily programmable in parallel; initial tests indicate nearly linear scaling with the number of processors. Other advanced techniques, such as multipole acceleration, can be applied as well. The semi-analytical method for desingularization tensors is similarly conducive to parallelization. Finally, the two techniques are not mutually exclusive; particles may be defined in a piecewise fashion where tubular or otherwise axisymmetric sections utilize the semi-analytical method, and the junctions of these sections are treated with the multimesh method. For example, a rectangular grid can be constructed in this way, as is commonly used for large-scale models of fibrous media or membranes.
2.A Axisymmetric desingularization: mathematical and technical details

Closed-form expressions for the integrals of $G_2$ and $\Psi$ over a circular circumference are provided, using the notation and geometry of figure 2.2. In what follows, $\Delta^2 = 1 - k^2 \sin^2 \phi$.

2.A.1 Closed-form azimuthal integration for $G_2$

Azimuthal integrals for the single layer have been provided in different forms, e.g., by Lee & Leal (1982), and are included here for completeness. All terms of the integrand of $G_2$ integrated over a circle have the form:

$$\int_{-\pi}^{\pi} r_i r_j \frac{d\psi}{r^3} = 4c_0^3 \int_0^{\pi/2} \frac{r_i r_j}{\Delta^3} d\phi, \quad (2.17)$$

where $c_0 = ((\rho + \rho_0)^2 + (z - z_0)^2)^{-1/2}$ and $\phi = \psi/2$. Terms that represent odd functions, such as $r_1r_2$, are zero in the special basis. Nonzero terms are provided below.

$$r_1r_1 = 4\rho^2 \cos^4 \phi + 4\rho(\rho_0 - \rho) \cos^2 \phi + (\rho_0 - \rho)^2 \quad (2.18)$$
$$r_1r_3 = (z - z_0)(\rho(2\cos^2 \phi - 1) + \rho_0) \quad (2.19)$$
$$r_2r_2 = 4\rho^2 \sin^2 \phi \cos^2 \phi \quad (2.20)$$
$$r_3r_3 = (z - z_0)^2 \quad (2.21)$$

2.A.2 Closed-form azimuthal integration $\Psi$

All terms of the azimuthal integration for $\Psi$ have the form:

$$\int_{-\pi}^{\pi} r_i r_j r_k \frac{d\psi}{r^5} = 4c_0^5 \int_0^{\pi/2} \frac{r_i r_j r_k}{\Delta^5} d\phi, \quad (2.22)$$
where $r_n = r \cdot n(x)$. The nonzero terms of this symmetric third-rank tensor are provided below, where $\delta_z = z - z_0$.

\[
\begin{align*}
    r_n r_1 r_1 &= 16 \rho^3 \rho_0 n_\rho \cos^3(\phi) \\
                   &+ 8 \rho^2 \cos(\phi) \left( (\rho^2 - 4 \rho_0 \rho + 3 \rho_0^2) n_\rho + \rho n_\delta_z \right) \\
                   &- 12 \rho (\rho - \rho_0) \cos^4(\phi) \left( (\rho - \rho_0)^2 n_\rho + \rho n_\delta_z \right) \\
                   &+ 2 (\rho - \rho_0)^2 \cos^2(\phi) \left( (3 \rho^2 - 4 \rho_0 \rho + \rho_0^2) n_\rho + 3 \rho n_\delta_z \right) \\
                   &- (\rho - \rho_0)^3 ((\rho - \rho_0) n_\rho + n_z \delta_z) \\

    r_n r_1 r_3 &= 8 \rho^2 \rho_0 n_\rho \delta_z \cos^6(\phi) \\
                   &+ 4 \rho \delta_z \cos^4(\phi) \left( (\rho^2 - 3 \rho_0 \rho + 2 \rho_0^2) n_\rho + \rho n_\delta_z \right) \\
                   &- 2 (\rho - \rho_0) \delta_z \cos^2(\phi) \left( (2 \rho^2 - 3 \rho_0 \rho + \rho_0^2) n_\rho + 2 \rho n_\delta_z \right) \\
                   &+ (\rho - \rho_0)^2 \delta_z ((\rho - \rho_0) n_\rho + n_z \delta_z) \\

    r_n r_1 r_2 &= 16 \rho^3 \rho_0 n_\rho \sin^2(\phi) \cos^6(\phi) \\
                   &+ 8 \rho^2 \sin^2(\phi) \cos^4(\phi) \left( (\rho - \rho_0)^2 n_\rho + \rho n_\delta_z \right) \\
                   &- 4 \rho^2 (\rho - \rho_0) \sin^2(\phi) \cos^2(\phi) \left( (\rho - \rho_0) n_\rho + n_z \delta_z \right) \\

    r_n r_3 r_3 &= 4 \rho \rho_0 n_\rho \delta_z^2 \cos^4(\phi) \\
                   &+ 2 \delta_z^2 \cos^2(\phi) \left( (\rho - \rho_0)^2 n_\rho + \rho n_\delta_z \right) \\
                   &- (\rho - \rho_0) \delta_z^2 ((\rho - \rho_0) n_\rho + n_z \delta_z)
\end{align*}
\]
\[ r_n r_2 r_3 = 8 \rho^2 \rho_0 n_\rho \delta_z \sin^2(\phi) \cos^4(\phi) \]
\[ + 4 \rho^2 \delta_z \sin^2(\phi) \cos^2(\phi) ((\rho - \rho_0) n_\rho + n_z \delta_z) \]
\[ r_n r_3 r_3 = 2 \rho_0 n_\rho \delta_z^2 \cos^2(\phi) + \delta_z^2 ((\rho - \rho_0) n_\rho + n_z \delta_z) \] (2.27)

2.A.3 Integrals of \( \Delta \)

Here is a list of required integrals involving \( \Delta \), reduced to elliptic integrals:

\[ \int_0^{\pi/2} \frac{d\phi}{\Delta} = F, \quad \int_0^{\pi/2} \Delta d\phi = E, \quad \int_0^{\pi/2} \frac{d\phi}{\Delta^3} = \frac{E}{1 - k^2}, \] (2.29)

\[ \int_0^{\pi/2} \Delta^3 d\phi = \frac{1}{3} [(4 - 2k^2)E - (1 - k^2)F], \] (2.30)

\[ \int_0^{\pi/2} \frac{d\phi}{\Delta^5} = \frac{(4 - 2k^2)E - (1 - k^2)F}{3(1 - k^2)^2}, \] (2.31)

where \( F \) and \( E \) are complete elliptic integrals of the first and second kind, respectively, with modulus \( k \).

2.A.4 Fast-convergent calculation of elliptic integrals

The complete elliptic integrals \( F \) and \( E \) can be calculated very efficiently, and to machine precision, by the fast-convergent relations (Davis, 1962):

\[ F = \frac{\pi}{2} (1 + K_1)(1 + K_2)(1 + K_3) \ldots, \quad E = \left(1 - \frac{k^2}{2}P\right)F \] (2.32)

where

\[ K_0 = k, \quad K_p = \frac{1 - C}{1 + C}, \quad C = \sqrt{1 - K_p^{p-1}} \] (2.33)
and

\[ P = 1 + \frac{K_1}{2} \left( 1 + \frac{K_2}{2} \left( 1 + \frac{K_3}{2} \left( \ldots \right) \right) \right). \]  

(2.34)

Based on (2.29-2.31), the necessary integrals involving powers of \( \Delta \) and \( \cos \phi \) can be calculated recursively (Gradshteyn & Ryzhik, 2014). From the definition of \( \Delta \), first note that

\[ \sin^2 \phi = \frac{1 - \Delta^2}{k^2}, \quad \cos^2 \phi = 1 - \frac{1 - \Delta^2}{k^2} = \frac{k^2 - 1 + \Delta^2}{k^2}. \]  

(2.35)

Letting

\[ J^m_n = \int_0^{\pi/2} \Delta^m \cos^{2n} \phi \, d\phi, \]  

(2.36)

then

\[ J^{n+1}_m = (1 - 1/k^2) J^n_m + \frac{J^{n+2}_m}{k^2}. \]  

(2.37)

So, only four integrals are required to recursively calculate the remaining terms involving \( \Delta \) and powers of cosine:

\[ \Delta^p \cos^2 \phi = \left( 1 - \frac{1}{k^2} \right) \Delta^p + \frac{\Delta^{p+2}}{k^2}, \quad \text{for} \ p = \{-1, -3, -5\}, \]  

(2.38)

and

\[ \frac{\cos^4 \phi}{\Delta} = \left( \frac{\Delta^3}{k^4} + \frac{2(k^2 - 1) \Delta}{k^4} \right) + \left( \frac{(k^2 - 1)^2}{k^4 \Delta} \right). \]  

(2.39)
Figure 2.15: Coordinated adaptive resolution of a small mesh. The original mesh (black) is subject to a user-provided criteria for subdivision, assumed to be satisfied by the triangles highlighted in cyan. How new edges (in grey) are added depends on if a neighboring triangle will be subdivided.

2.B Coordinated triangle subdivision

A straightforward extension of a simple triangle subdivision scheme allows for obtaining four-times-denser meshes within contiguous regions. As shown in figure 2.15, all edges of triangles that meet a given criteria are subdivided at their midpoints. If a neighboring triangle is also being subdivided, connectivity between the added nodes is updated accordingly. Otherwise, an edge is added between an added node and an existing node (typically, only around the perimeter of a contiguous region). With respect to programming, the method involves considerably more bookkeeping compared to subdividing and relaxing individual triangles one at a time. However, this coordinated triangle subdivision did not require relaxation of the resulting mesh, and was invaluable when much higher mesh densities were required within certain spatial regions. Since the base mesh is unaffected, added nodes can subsequently be removed, and the result is again a high-quality mesh. In this way, the region of high-density nodes can remain spatially fixed as a mesh moves through it. Finally, by initializing added nodes with interpolated values of all quantities used by the boundary-integral calculations, adding new nodes did not appreciably slow down convergence during GMRES iterations.
Chapter 3

Internal circulation and mixing within tight-squeezing deformable droplets

You cannot see the changes that you’re dreaming about, because they’re internal.

-Alice Walker

Synopsis

The internal flow and mixing properties inside deformable droplets, after reaching steady state within two types of passive droplet traps, are visualized and analyzed as dynamical systems. The first droplet trap (constriction) is formed by three spheres arranged in an equilateral triangle, while the second consists of two parallel spherocylinders (capsules). The systems are assumed to be embedded in a uniform far-field flow at low Reynolds number, and the steady shapes and interfacial velocities of the drops are created using the boundary-integral method. The internal velocity field is recovered by solving the internal Dirichlet problem, also via a desingularized boundary-integral method. Calculation of 2D streamlines within planes of symmetry reveals internal fixed points of the flow. The type of each fixed point is classified in 3D and their interactions probed using passive tracers and their Pioncaré maps. For the two-capsule
droplet, attracting and repelling focus saddles located on orthogonal symmetry planes influence the regular flow within the drop. For the three-sphere droplet, large regions of chaos are observed, embedded with simple periodic orbits. Flow is visualized via passive dyes, using material lines and surfaces. In 2D, solely the interface between two passive interior fluids is advected using an adaptive number of linked tracer particles. The reduction in dimension decreases the number of required tracer points, and also resolves arbitrarily-thin filaments, in contrast to backward cell-mapping methods. In 3D, the advection of a material surface, bounded by the droplet interface, is enabled using an adaptive mesh scheme. Off-lattice 3D contour advection allows for highly-resolved visualizations of the internal flow and quantification of the associated degree of mixing. Analysis of the time-dependent growth of material surfaces suggests the three-sphere droplet exhibits greater complexity than the two-capsule droplet, further supporting the conclusion that this three-fold-symmetric system has superior mixing properties.

3.1 Existing methods for the visualization and quantification of mixing

As droplets are used for increasingly-precise tasks, such as microreactors in microfluidic systems, it has become more important to understand how the confinement geometry affects their internal flow. For example, certain microfluidic designs include arrays of static droplet traps to enable reactive mixing for a set residence time, before releasing the drops by reversing the flow direction (Huebner et al., 2009). Interesting optimization questions arise: do certain droplet-trap shapes increase the degree of mixing? What is the effect of introducing asymmetry into the droplet trap? Computational tools have the potential to screen a large number of geometries to help answer these questions, both to estimate the amount of mixing and for precise determination of properties of the internal velocity field, such as the topology and complexity of the flow.

Mixing is notoriously slow in the low-Reynolds-number (Stokes) regime, at which most microfluidic devices operate, but chaotic advection has been shown to greatly increase mixing (Ottino, 1990). Time-dependent perturbations in the flow provide a straightforward way to introduce chaos, as
traditionally demonstrated by the blinking vortex model (Aref, 1984; Aref et al., 2002). However, chaos has also been demonstrated to occur in steady 3D Stokes flows, as originally reported by Bajer & Moffatt (1990) for a quadratic flow within a spherical domain that exhibits stretch-twist-fold chaotic dynamics. Subsequently, Stone et al. (1991) provided a simpler example of chaos inside a spherical droplet subject to linear Stokes flows. Properties of these flows can be quantified within the mathematical framework of dynamical systems. The traditional tool used to visualize the flow of these systems is the Poincaré section, though more recently other numerical tools (e.g., topological structure) as well as additional measures from chaos theory (e.g., Lyapunov exponents, see Boffetta et al. (2001) and Ottino et al. (2004)) have become prevalent. The numerical determination of topological structures, such as fixed points and periodic orbits, and the relationships between them, can be derived from discrete Morse theory (Forman, 2002) or by analysis of the gradient field (Weinkauf, 2008).

More direct dynamic visualizations of mixing are important both for experimental and numerical studies. Microfluidic drops can be mixed during flow by serpentine channels (Madadelahi & Shamloo, 2017; Abbyad et al., 2011) or by introducing irregular obstructions into the channel (Jana et al., 1994a). Internal flows are often visualized by the passive advection of dye, e.g., initially filling one half of the drop (Bringer et al., 2004; Song & Ismagilov, 2003), or by particle image velocimetry (Oishi et al., 2011; Liu et al., 2019). Visualizations of numerical simulations borrowed these ideas directly: passive tracers are used to plot 3D trajectories and map out Poincaré sections (Xu & Homsy, 2007), or ‘blobs’ of passive dye are simulated by advecting ‘material volumes’ (Speetjens et al., 2004). An issue arises when these material volumes are composed of many passive particles imagined to have finite size. Although the blob initially appears contiguous, eventually, the constituent particles will separate enough that the blob no longer appears connected, even when the Hamiltonian nature of the flow technically prevents such a topological transformation. Even though, given sufficient tracer particles, this simple method often provides an adequate picture of the flow, and can even mirror experimental images due to the break-up of thin filaments under capillary instability, more exacting methods are required to maintain high resolution at longer times (Szalai et al., 2004). For example, the backward Poincaré cell-map method utilizes fixed cells instead of mobile tracers, and results in considerably less noise during material advection when applied to
Arbitrary resolution can be achieved by explicitly tracking the evolving interface, e.g., with a line of connected tracers. This concept seems to have been introduced independently in application to inviscid flows, where it is known as contour advection (Zabusky et al., 1979; Dritschel, 1988; Waugh & Plumb, 1994), and for creeping flow in application to a driven cavity, where it is known as a material line (Franjione & Ottino, 1987; Jana et al., 1994b). A potentially significant drawback, even with modern computing power, is that material lines in chaotic flow grow exponentially (Fung & Vassilicos, 1991). On the other hand, this hallmark of chaos can therefore be arbitrarily resolved and readily computed using the material line method. For example, the rate of growth of such lines is related to a useful measures such as the topological entropy (Thiffeault, 2004; Candelaresi et al., 2017). Retaining connectivity between tracers can also reveal topological properties of the flow in a robust manner (Boyland et al., 2000; Thiffeault & Finn, 2006). From a numerical standpoint, the local resolution of material lines can by maintained by simply inserting an additional tracer between nodes that exceed a prescribed separation, or by more advanced methods that account for curvature of the line or allow for splitting and reconnection (surgery) of the line.

Advection of a passive dye, or material blob, provides quantitative information about mixing efficiency when a measure for the degree of mixing is defined. Many such measures to quantify mixing have been proposed. Metrics include thickness of the striated layers of the dye or fractal dimension of its interface (Ottino, 1990), stretching statistics or particle spread (Liu et al., 1994; Florek & Tucker, 2005), or the average distance between each point in one fluid dye to the other (Stone & Stone, 2005). Perhaps this final metric is particularly suited for simple analysis of either experimental or numerical images that can be converted into two-color images, where pixels provide a ‘natural’ discretization of the field. In all cases, the goal is to convert a time-series of flow snapshots (typically assumed to be nondiffusive) into a scalar that is indicative of how well-mixed the fluid is, i.e., how quickly diffusion can result in a completely homogeneous fluid. Finn et al. (2004) provided a direct comparison between many classes of mixing metrics and demonstrated that they are not always well-correlated, which emphasizes that determining a suitable measure often requires a case-by-case evaluation.

In the present work, we use many of the above tools to provide a comprehensive picture of the
internal flow and mixing in deformable droplets trapped in two simple types of constrictions, one comprised of capsules with two-fold symmetry, and the other of spheres with three-fold symmetry. The configuration of these constrictions and details on how the systems were created are provided in §2. The desingularized boundary-integral formulation used to solve the internal Dirichlet problem and recover the internal velocity field is presented in §3. Numerical and technical details regarding how passive tracers and material lines and surfaces were advected and visualized are given in §4. Particular technical challenges were presented when the material surface, advected in three dimensions, was assumed to be bounded by an arbitrary, dynamic loop on the droplet interface. The explicit 3D advection and visualization technique presented herein offers high-resolution qualitative and quantitative insight into the internal dynamics of these confined systems. In §5, the internal flow within the two trapped droplets is analyzed from a dynamical systems standpoint and visualized using passive tracers and dyes, and the two droplets’ relative strength as mixers is characterized. Concluding remarks are provided in §6.

3.2 Problem formulation: creation of the steady-state droplets

Consider a deformable droplet that has entered a constriction composed of solid particles and become trapped indefinitely. The system properties (notably the capillary number) required for such an occurrence have been the subject of previous work, using assumptions that the droplet is freely-suspended in a far-field flow, both the drop and carrier fluids are Newtonian, and the solid particles are fixed in space (Zinchenko & Davis, 2006; Gissinger et al., 2020). Assuming the system remains embedded in the far-field flow, the internal velocity field of the stationary, trapped droplet is steady-state and nontrivial. Provided only the interfacial velocity and shape of the droplet, the internal velocity field can be recovered using the boundary-integral method, and its mixing and topological properties analyzed.

Two simple constrictions are considered, one composed of spheres and with three-fold symmetry, and another made up of capsules and having two-fold symmetry. The characteristic length $L$ of the systems are the radii of the sphere or capsule, respectively, as shown in figure 3.1. For the three-sphere constriction, the critical capillary number (the capillary number (defined below) below which the drop becomes trapped)
was determined to be $Ca_{crit} \approx 1$ for a droplet with a dimensionless non-deformed radius of $\tilde{a} = 0.6$ and a gap between spheres of $\epsilon = 0.25$, using the boundary-integral method as discussed at length by Zinchenko & Davis (2006). Therefore, $Ca = 0.9$ is subcritical, and the resulting trapped drop is shown in figure 3.1a after slowing to a dimensionless velocity (averaged over the drop volume) of magnitude $U < 1 \times 10^{-4}$, four orders of magnitude smaller than the magnitude of the far-field velocity $|u_\infty| = 1$. The solid-particle mesh resolution (total number of triangles comprising the surface) is $\tilde{N} = 11520$, and the drop-resolution is $\tilde{N} = 20480$. This resolution for the droplet is higher than those used by Zinchenko & Davis (2006), and was chosen to increase the accuracy of the computed internal velocity field. A plot of drop velocity vs. for a (clean) droplet at this resolution is provided by Gissinger et al. (2019a), figure 8 therein. For the two-capsule constriction, a capillary number of $Ca = 0.7$ was found to be subcritical, for drop radius $\tilde{a} = 0.5$, capsule length $L = 6$ and minimum separation between capsules of $\epsilon = 0.5$ (Gissinger et al., 2020), as shown in figure 3.1b. For both systems, the viscosity ratio of droplet and external fluids is $\lambda = 4$, although the critical capillary number is not sensitive to this value. Additional simulation details for both systems are provided in their respective papers.

All reported values are made non-dimensional using the far-field velocity and characteristic length of each system. The velocity and times scales are $|u_\infty|$ and $L/|u_\infty|$, respectively. The capillary number is defined as

$$Ca = \frac{\mu_e |u_\infty|}{\sigma} \frac{\tilde{a}}{L},$$

(3.1)

where $\mu_e$ is the external medium viscosity and $\sigma$ is the constant surface tension of the drop interface.

The ‘drop centre’ is mentioned frequently below, and is defined as the surface centroid of the drop interface,

$$x_c = \frac{1}{S} \int_S x \, dS_x.$$  

(3.2)

As a fraction from the bottommost point of the drop to the topmost (in reference to the $z$-axis in figure 3.1), the surface centroid occurs at 0.56 for the three-sphere droplet, and 0.52 for the two-capsule droplet.
Figure 3.1: Side and top views of two trapped-droplet systems embedded in a far-field flow (of uniform velocity $u_\infty$) and with characteristic length $L$. (a) A droplet ($\tilde{a} = 0.6$) trapped between three spheres ($Ca = 0.9$, $\lambda = 4$, $\epsilon = 0.25$). (b) A droplet ($\tilde{a} = 0.5$) trapped between two capsules ($Ca = 0.7$, $\lambda = 4$, $\epsilon = 0.5$, $L = 6$).
3.3 Calculation of the internal velocity field

Once a trapped state is simulated with the interfacial velocity \( u_S \) on the drop surface, as outlined in the previous section and detailed elsewhere (Zinchenko & Davis, 2006; Gissinger et al., 2020), the next task is to restore the fluid velocity field inside the drop. The matching viscosities case is much simpler in this respect, since for \( \lambda = 1 \) equation 2.3 is valid for the entire fluid domain, thus providing the velocity field within the droplet. For a general \( \lambda \neq 1 \), though, the fluid velocity inside the drop must be recovered from an additional solution of the internal Dirichlet problem for Stokes flow with prescribed boundary values \( u = u_S \) on \( S \).

Following the general theory (Pozrikidis, 1992; Power & Wrobel, 1995; Brebbia et al., 2012; Kim & Karrila, 2013), the flow strictly inside the drop can be sought as a double-layer potential

\[
\mathbf{u}(\mathbf{y}) = 2 \int_{S} \mathbf{Q}(\mathbf{x}) \cdot \mathbf{\tau}(\mathbf{r}) \cdot \mathbf{n}(\mathbf{x}) \, d\mathbf{S}_{x},
\]

(3.3)

where \( \mathbf{Q} \) is an unknown density function (not to be confused with \( \mathbf{q} \) in Section 3). Upon taking the limit \( \mathbf{y} \to S \) and the substitution ("Wielandt’s deflation for a container") \( \mathbf{Q} = \mathbf{W} - \mathbf{W}'/2 \) (where, again, prime indicates rigid-body projection conveniently calculated by the recipe in Zinchenko et al. (1997)), a fully-deflated boundary-integral equation is obtained for \( \mathbf{W} \):

\[
\mathbf{W}(\mathbf{y}) = -2 \int_{S} \mathbf{W}(\mathbf{x}) \cdot \mathbf{\tau}(\mathbf{x} - \mathbf{y}) \cdot \mathbf{n}(\mathbf{x}) \, d\mathbf{S}_{x} + \mathbf{W}'
- \frac{\mathbf{n}(\mathbf{y})}{S} \int_{S} \mathbf{W} \cdot \mathbf{n} \, d\mathbf{S} + \mathbf{u}_S(\mathbf{y}) \quad \text{for } \mathbf{x}, \mathbf{y} \in S
\]

(3.4)

with the unique solution and the spectral radius less than one, suitable for iterative solution by the simplest method of successive substitutions.

In numerical implementation, standard desingularization of the double-layer integral in (3.4) is achieved with the subtraction

\[
-2 \int_{S} \mathbf{Q}(\mathbf{x}) \cdot \mathbf{\tau}(\mathbf{r}) \cdot \mathbf{n}(\mathbf{x}) \, d\mathbf{S}_{x} = -2 \int_{S} [\mathbf{Q}(\mathbf{x}) - \mathbf{G}(\mathbf{y})] \cdot \mathbf{\tau}(\mathbf{r}) \cdot \mathbf{n}(\mathbf{x}) \, d\mathbf{S}_{x} - \mathbf{Q}(\mathbf{y}).
\]

(3.5)
The tolerance for iterative solution of (3.4) was set to $10^{-8}|u_\infty|$.

3.4 Visualization of the internal velocity field

3.4.1 Numerical methods

Passive tracers were advected using the fourth-order Runga-Kutta method using a time step of $\Delta t = 1$. Note that the maximum dimensionless velocity within either trapped drop is $\approx 0.01$. Using a time step two orders of magnitude smaller, $\Delta t = 0.01$, with either Runga-Kutta or a simple Euler integration, resulted in visually indistinguishable trajectories, e.g., for the complex orbits discussed in §3.5. When advecting a material line, a line of tracers, connected in serial by edges of length $l_e = 0.01$, was initialized between two given points, e.g., on the drop interface. When any edge length exceeded $l_e$, the edge was bisected by adding another tracer. When an edge length dropped below $l_e/2$, its two nodes were merged. When the material line was assumed to lie on a plane of symmetry, all the nodes were projected onto the plane after every time step to correct for numerical drift.

Advection of a material surface closed by an arbitrary boundary, in this case confined to the droplet
interface, presented several conceptual and programming challenges. Here, we outline the method at a conceptual level. First, the closed loop that forms the material surface’s boundary was advected by interpolating the interfacial velocity field (alternatively, the boundary-integral problem could be solved for points located on the surface). This boundary-loop is useful for both visualization, e.g., when assuming that half of the droplet is initially filled with a passive dye, and for several of the operations that maintain the quality of the material-surface mesh (described below). The resolution of this 1D boundary-loop was maintained in a similar manner as that of the material line described above. Namely, a default edge length \( l_e = 0.01 \) was defined, and edges were bisected if exceeding \( l_e \) and collapsed if less \( l_e/2 \). These strict criteria maintained high resolution of the relatively few nodes that were part of the boundary-loop. After choosing a planar cross-section of the drop to advect, the initial material surface was constructed by a starting with a simple, excessively-large mesh of equilateral triangles of edge length \( l_e \), and deleting triangles that overlap with the exterior of the boundary-loop (determined via the winding number algorithm). Until the visualization stage, the boundary-loop was not connected to the interior of the material surface. A second important loop consists of the edges that bound the material surface within the drop interior (i.e., not on the drop interface), which we will refer to as the edge-loop. If the edge-loop was advected to within \( l_e/2 \) of the boundary-loop, nodes were deleted from the edge-loop (and a new edge-loop determined). Similarly, if an edge-loop node receded at least \( 2l_e \) from the boundary-loop, additional triangles were added to material surface. Specifically, a new edge of length \( l_e \) was extended from the receding edge-loop node, such that it bisected the two adjacent edge-loop edges, and its location was then improved based on an interpolation with nearby boundary-loop nodes. Finally, the quality of the entire material surface mesh was maintained adaptively using a simple edge-length based criteria. Edges were bisected (and additional edges and triangles created to maintain a triangulated mesh) if they exceeded \( 2l_e \), and edge nodes were merged if within \( l_e/2 \). This simple adaptive mesh scheme does not enforce a limitation on the number of edges per node, but in practice it resulted in a maximum edges-per-node of about 10. Since there were no per-node quantities to calculate for this passive mesh, there was no technical requirements regarding a minimum or maximum number of first neighbours.

Finally, the advected material surface must be visualized, keeping in mind that the aspect of interest
is the interaction between the two volumes that it separates within the drop. First, the strip between the
edge-loop and the boundary-loop is triangulated. As shown in figure 3.2, at any given time step, we then
have a surface that is bounded by the drop interface. The surface is used to carve out two distinct volumes
(a feature available in Blender v2.78). These two parts of the drop interior can then be rendered with
different colors, to mimic translucent dye. Furthermore, these closed meshes representing each dye are
utilized by quantitative measures of the degree of mixing. For example, the surface area of a triangulated
mesh is easily calculated by simply summing over all triangle areas.

3.4.2 Potential sources of error

Studying possibly chaotic dynamical systems numerically is always subject to the degrading effect of
round-off errors over long times. However, additional systematic errors can arise when the boundary
conditions (in the present case, shape and velocity of the drop interface) are also not known analytically. In
the present case, e.g., symmetry breaking (see §3.5, figure 3.7) can occur, caused by slight offsets of the
droplet from the centre of symmetric systems, which would have developed as the droplet approached the
particles from its initial upstream position (see Gissinger et al. (2020) for a discussion of how such effects
were mitigated). Additionally, although the boundary-integral equations can be solved with
arbitrarily-high precision, their singular nature becomes problematic as tracers approach the drop
interface. Without refinement of the \( \hat{N}_\Delta = 20K \) resolution droplet meshes used above, small but clearly
non-physical perturbations of trajectories occur within distances of \( \approx 0.005 \) of the interface (using the
simple singularity subtraction of equation 3.5). These ‘singularity perturbations’ can have subtle but
important effects when calculating dynamics; for example, if tracers always tend to be ‘kicked’ away from
the interface at a given point, apparent periodic orbits can be observed that are in fact numerical artifacts
rather than representative of the exact system dynamics. Finally, it was not uncommon for trajectories to
switch between regions separated by symmetry planes. Reducing the time step by two orders of magnitude,
\( \Delta t = 0.01 \), did not reduce or promote this behavior. It is unclear if this basin-hopping was primarily
caused by the actual system dynamics, numerical asymmetries in the boundary conditions, and/or inherent
limitations of the classic Runge-Kutta scheme.
3.5 Internal droplet circulation: numerical results

3.5.1 2D streamlines on symmetry planes

Streamlines for the internal velocity field of droplets trapped in three-sphere and two-capsule constrictions are shown in figure 3.3. Planes of symmetry were used to create cutaways of each drop for visualization; a quadrant and a sixth are sliced out of the two-capsule and three-sphere constrictions, respectively. Planes of symmetry are good candidates for fixed points of the 3D velocity field, and one fixed point is observed on each of the cutaway faces in figure 3.3 (highlighted with colored dots). The maximum interior dimensionless velocity is \( \approx 0.01 \), and occurs at the drop interface and away from solid-particle surfaces. For both drops, fixed points appear near the lower perimeter of the dimpled near-contact region (formed by lubrication interactions with the solid surface), and near to the drop interface. Also, fixed points appear away from the interface in the upper half of each drop. However, these apparently similar pairs of fixed points interact very differently in each of these systems. Not shown are fixed points that exist on the drop interface itself; for example, an obvious heteroclinic orbit within both drops is that between the bottom and the top of each drop, consisting of a simple vertical line along the intersection of the symmetry planes. Small perturbations of a tracer near symmetry planes can greatly affect its long-term dynamics, e.g., by causing it to switch between quadrants of the two-capsule drop.

3.5.2 Dynamics within the two-capsule droplet

In 3D, the labeled points in figure 3.3 are saddle points, and the interactions between such points help define the topological skeleton of the velocity field. As shown in figure 3.4, a tracer that starts in the two-capsule droplet near the green point flows to the orange point, implying that the green point is a repelling focus saddle and the orange point is an attracting focus saddle, using the definitions pictured in figure 3.4. The trajectory of this tracer (bold black curve) closely approximates the heteroclinic orbit between these saddle points, at least until nearing the attracting focus saddle. Note that, with a small perturbation of the initial starting point, the tracer could instead flow to the other attracting focus saddle, following a mirror-image orbit within another quadrant. To help visualize how this orbit influences the
Figure 3.3: Cutaways of trapped drops reveal internal dynamics, with velocity magnitude shown in color. (a) A sixth, defined using planes of symmetry, is cut from the three-sphere droplet to reveal two-dimensional streamlines and fixed points (red and blue). (b) A quadrant is cut from the two-capsule droplet, revealing two fixed points (green and orange) on orthogonal symmetry planes.

internal flow, the trajectories of 100 tracers particles, all starting in one quadrant but near the drop centre, are also shown in color. When observing the time series of tracer trajectories within the two-capsule droplet, they are most obviously characterized by loops around the heteroclinic orbit within a given quadrant. In contrast, both of the fixed points within the three-sphere droplet are attracting saddle points, and the internal dynamics are quite different, as discussed below.

The combined Pioncaré sections of 100 tracers starting within 0.01 of each other near the centre of the two-capsule droplet are shown in black in figure 3.5a, where 3D trajectories are intersected with the $xy$-plane passing through the drop centre. The total duration of each trajectory is $5 \times 10^5$, resulting in $> 86000$ total points of intersection. The points within the blue region result from the one-time flow away from the repelling focus saddle, shown in 3.5b (also shown in figure 3.4). Shortly thereafter, the tracers tend toward regular orbits, as can be inferred from the Pioncaré map. One such characteristic orbit is shown in figure 3.5c, which shows a tracer just before entering the orbit. The orbit is visualized over a total trajectory duration of $> 2.5 \times 10^6$, and has a period of $\approx 1125$. It consist of 12 turns around the heteroclinic orbit, but despite its apparent complexity is a simple loop (i.e., an unknot, as determined by the method of Dorier et al. (2018)). Figure 3.5a also reveals an apparent island bordering the drop
Figure 3.4: Internal flow dynamics within a quadrant of the two-capsule droplet revealed by tracers. The heteroclinic orbit between a repelling focus saddle (green) and an attracting focus saddle (orange) is approximated by the bold black trajectory. In addition, 100 tracers starting near the drop centre (placed randomly inside a cube of side length 0.01), are shown in color. See figure 3.3 for location of saddle points with respect to the drop interface.
Figure 3.5: Visualizations of the flow within a quadrant of the two-capsule drop. Axes in \( \text{b} \) apply to entire figure. \((a)\) The Poincaré section for 100 tracers starting near the droplet centre, intersecting with the \( xy \)-plane that contains the drop centre (shown in black). Points within the blue section result from the trajectories shown in \( \text{b} \). The Poincaré map for a single tracer initiated within the ‘island’ is shown in orange. \((b)\) Another view of the trajectories shown in figure 3.4. \((c)\) An example of a complex periodic orbit, consisting of a loop with 12 turns around the heteroclinic orbit. \((d)\) The orbit of a single tracer initialized near the centre of the island in \( a \). Shaded to emphasize position along the \( z \)-axis. The Poincaré section of this trajectory is shown in orange in \( a \).

interface. A tracer manually placed within this island, away from its edges, results in a regular orbit that remains within a small region, as shown in 3.5\( d \). The Poincaré section for this orbit is also shown, in orange, in frame \((a)\). The tracer begins at the end of one of the spiral arms clearly visible in the Poincaré map; although not resolved due the finite size of the plotted intersection points, these spirals continue inward, converging toward a single point.
3.5.3 Dynamics within the three-sphere droplet

A similar analysis was completed for the three-sphere system, with notably different results. The combined Poincaré section for 100 tracers starting near the droplet centre is shown in figure 3.6a. The stochastic region filling most of the cross-section is a classic indicator of chaotic behavior, suggesting enhanced mixing for this three-fold-symmetric system as compared to the two-capsule drop. A large island is also revealed within each sixth of the droplet, which contains stable orbits, as was observed in each quadrant of the two-capsule drop. One such trajectory is calculated by randomly placing a tracer within the island, resulting in five-sided shapes comprising its Poincaré map (shown in figure 3.6a in orange). This stable trajectory is shown in 3D in figure 3.6b, and revealed to be a simple loop embedded in the upper part of the droplet. A portion of a chaotic trajectory is shown in light blue as it explores much of the surrounding space, including passing through the center of, and the around the perimeter of, the stable loop.

For the three-sphere droplet, both of the interior saddle points marked in figure 3.3 are attracting focus saddles. Tracers initialized at these points follow chaotic trajectories visually similar to that shown in figure 3.6b. Observations of chaotic tracers show that the saddle points interact with each other and themselves. For example, a tracer may flow toward the upper attracting focus saddle (the red point in figure 3.3), spiral outward and away from its symmetry plane, and then return, with this pattern repeating a number of times. When initializing a tracer at either of these saddles, and letting time run backward, the tracers end up at the top of the drop, after approaching the drop interface. This backward orbit highlights the important role of the fixed point at the top of the three-sphere drop, which resembles an attracting node saddle (in forward time). So, a class of common trajectories can be summarized: a tracer that approaches the centerline and ends up near the top of the drop, may flow toward any of the six attracting focus saddles, with a small perturbation. Aside from the bottom of the drop, other fixed points on the interface include another point corresponding to a source within the 2D surface, located at the center of the dimpled near-contact region, and a point of extensional flow above the dimple (see Gissinger et al. (2019a), figure 10a therein, for a visualization of this interfacial field). Based on observing time series of advected tracers, these features have less obvious effects on the internal dynamics. For example, a tracer starting near the centre of dimple, and run backward, first interacts with the nearby interior saddle point...
Figure 3.6: Dynamic behavior within the three-sphere droplet. (a) Intersections with the $xy$-plane containing the droplet centre, for 100 tracers initialized near the droplet centre, over a duration of $5 \times 10^5$ (shown in black). The Poincaré map of a single tracer initialized within the island is also shown in orange, over a trajectory of the same duration. Dotted green lines indicate planes of symmetry. (b) The non-chaotic orbit from frame (b) is shown, colored to indicate position along the $z$-axis. Also shown in light blue is part of a chaotic orbit (over a duration of $2 \times 10^4$). Two orthogonal views shown.

before flowing to the top of the drop.

3.5.4 Mixing within trapped droplets

The 2D flow within the axial symmetry plane of the two-capsule droplet is shown in figure 3.7.

Theoretically, all velocity components should lie within the plane, but to remove numerical drift from the velocity of the dye interface, which is calculated in 3D, tracers were projected back on the symmetry plane at each time step. The symmetry breaking between the two counter-rotating vortices is attributed to the drop being slightly offset from constriction center, and would be difficult to prevent for this dynamically-created system. The axial cross-section shown is almost circular (eccentricity of $\approx 0.27$), and so qualitative similarities to the flow within a sphere or circle is expected. For example, figure 3.7 is
Figure 3.7: Advection of a 2D passive dye within the axial symmetry plane of the two-capsule droplet, using the dye interface as a material line. The material line is initialized at the droplet centre.

analogous to the 2D flow within a circle discussed by Wang et al. (2001) (see figure 6 therein), despite their equations being derived for a very different situation (fully-developed flow in a slightly-curved pipe). In the present system, the interface is in motion; the filament that forms at the bottom of the droplet becomes arbitrarily thin over time, but resolving such features is a nonissue when using the material line method. Also, this embedded 2D field is clearly not divergence-free; e.g., it contains two sinks corresponding to the repelling focus saddle discussed above.

The advection of a 2D material surface within the two-capsule drop is shown in figure 3.8. As indicated by the streamlines in figure 3.3, the highest surface velocity occurs midway between the capsules, i.e., in the symmetry plane containing the 2D flow in figure 3.7. The interfacial velocity field pinches the boundary of the material surface toward the circular perimeter, and pushes the upper half (red dye) of the drop first outward and downward, then inward and upward. The lack of persistent thin layers between the two dyes is one qualitative indication of relatively poor mixing in the system over this time period. The material surface closely approaches the droplet interface in several locations, especially just above the dimpled near-contact region; selected smoothing of the material surface is done for visualization purposes, as a post-processing step. Advancing beyond $t \approx 650$ would require additional improvements to the
Figure 3.8: Advection of a passive material surface within the two-capsule droplet (solid particles hidden). The initial surface lies on the $xy$-plane passing through the drop centre. Images are created using the procedure described in figure 3.2, which corresponds to $t = 25$. At $t = 650$, the material surface consists of $\approx 48$ K nodes ($\approx 95$ K triangles).
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Figure 3.9: Advection of a passive material surface within the three-sphere droplet (solid particles hidden). The initial surface lies on the $xy$-plane passing through the drop centre. For $t > 225$, half the droplet is hidden to reveal the internal dynamics (the full droplet is shown as the smaller image at $t = 325$). Visually, this three-fold-symmetric system appears considerably more mixing than that of the two-capsule droplet, including the formation of thin layers of each ‘dye’ by $t = 500$. At $t = 500$, the material surface consists of $\approx 150$ K nodes ($\approx 300$ K triangles).

Meshing scheme, e.g., curvature-adaptive edge length criteria to resolve the thin filament evolving toward the bottom of the drop.

Advection within the three-sphere droplet is shown in figure 3.9. Upward flow occurs at the centre of the drop and more slowly in the near-contact region, and downward flow closer to the interparticle interstices. The material surface quickly increases in complexity, so a cross-sectional cut using one symmetry plane is used for $t > 225$, to reveal the internal dynamics. The development of thin layers between the material surface evidences good mixing, e.g., visible near the center of the drop at $t = 500$. The stretch-and-fold motif, often cited as a model of chaos, is more obvious for the three-sphere droplet, with stretching of the material surface as it flows toward the top of the drop, and folding (and stretching)
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Figure 3.10: Growth of the material surfaces shown in figures 3.8 and 3.9 as a function of time. The rate of increase is a measure of system complexity, an indication of the superior mixing properties of the three-sphere system.

as it returns along the interface back toward the bottom. As discussed by Giona & Adrover (2001), the growth rates of material lines and surfaces follow the same scaling, i.e., both are related to the topological entropy of the system. So, the relative complexities of the two systems can be quantified by the rate of increase of the material surface area: over the initial duration of 600, the average rate was $2.7 \times 10^{-2}$ for the three-sphere droplet and $5.5 \times 10^{-3}$ for the two-capsule drop. As shown in figure 3.10, the surface area vs. time relationship appears to be piecewise linear. For the three-sphere droplet, the sharp increase in the rate ($t \approx 160 - 180$) corresponds to the surface initially reaching the top of the drop; it could be interesting to probe whether an exponential regime is attained when the duration spans many stretch-and-fold cycles, as thin layers between the material surface accrue.
3.6 Remarks on visualizing and quantifying mixing within 3D droplets

The internal flows of deformable droplets after reaching steady state within two types of passive droplet traps, modeled by three-sphere and two-capsule constrictions, are examined. The systems were previously created using the boundary-integral method, for which initial velocity data are available solely at the drop interface. In the present work, the interior velocity fields were recovered by solving the internal Dirichlet problem, also with a desingularized boundary-integral method using the double-layer formulation. Standard tools from dynamical systems theory, such as integral curves and Poincaré maps, are utilized to reveal the topological structure and properties of each system. Non-diffusive mixing within each droplet is visualized and quantified by advection of linked tracer particles. For example, in 2D, the material line that bounds two passive dyes is explicitly tracked using an adaptive number of tracers. In 3D, a procedure is introduced for advecting material surfaces bounded by arbitrary, time-dependent closed curves, and this 3D contour advection is used to visualize both chaotic and regular mixing within droplets.

Interior fixed points on the symmetry planes of each flow are identified to be focus saddles. In both cases, two interior saddle points are located on each symmetry plane, with one saddle point in the upper half of the droplet, and the second one just below the dimpled region nearly coating the solid particles. However, these apparently similar configurations give rise to very different flow dynamics. For the two-capsule droplet, the upper saddle point is a repelling focus saddle, and the lower is an attracting focus saddle. The heteroclinic orbit between these fixed points influences the flow dynamics, which include complex but regular orbits. The analogous fixed points within the three-sphere droplet are both attracting focus saddles. A Poincaré section at the centre of the three-sphere droplet, created by tracers starting near the drop centre, reveals chaotic behavior throughout most of the droplet. Finally, the mixing within both droplets is visualized using material lines and surfaces, which bound two passive dyes each initially filling one half of the drop. Qualitative observations suggest that the three-sphere system has greater tendency to create finely-striated layers between the dyes. The higher rate of growth of the material surface within the three-sphere droplet vs. the two-capsule droplet reinforces the conclusion that the three-sphere
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configuration results in a more effective droplet mixer.

Confined, deformable droplets swept along by a carrier fluid are a common occurrence in the physical world. The juxtaposition between this easily realizable, and comprehensible, system and its complex dynamics makes for an interesting study, and its analysis is only limited by dynamical systems theory and related fields. For example, slightly more advanced classifications of the interior flow could include identification of all elliptic, hyperbolic, etc. points, as well as calculation of Lyapunov exponents. Several direct extensions of the current work are also possible. All techniques used herein can be applied to transient drops, e.g., undergoing periodic motion. More experimentally-practical systems could include droplets within channels. Due the highly-sensitive nature of chaotic trajectories and their tendency to approach the drop interface, future studies of mixing in deformable droplets should consider more advanced desingularization or interpolation techniques, such as quadrature by expansion. Also, a curvature-adaptive mesh resolution would be helpful, allowing for the resolution of arbitrarily-thin 3D filaments while also decreasing the computational requirements of low-curvature regions of the material surface.
Chapter 4

A single drop with insoluble surfactant squeezing through spherical particles

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I found I could say things with color and shapes
that I couldn't say any other way -

-things I had no words for.

-Georgia O’Keeffe

Synopsis

The interfacial behavior of surfactant-laden drops squeezing through tight constrictions in a uniform far-field flow is modeled with respect to capillary number, drop-to-medium viscosity ratio and surfactant contamination. The surfactant is treated as insoluble and non-diffusive, and drop surface tension is related to surfactant concentration by a linear equation of state. The constriction is formed by three solid spheres
CHAPTER 4. SINGLE DROP SQUEEZING WITH INSOLUBLE SURFACTANT

held rigidly in space. A characteristic aspect of this confined and contaminated multiphase system is the rapid development of steep surfactant-concentration gradients during the onset of drop squeezing. The interplay between two physical effects of surfactant, namely the greater interface deformability due to decreased surface tension and interface immobilization due to Marangoni stresses, results in particularly rich drop-squeezing dynamics. A three-dimensional boundary-integral algorithm is used to describe drop hydrodynamics, and accurate treatment of close squeezing and trapped states is enabled by advanced singularity subtraction techniques. Surfactant transport and hydrodynamics are coupled via the surface convection equation (or convection-diffusion equation, if artificial diffusion is included), the interfacial stress balance, and a solid-particle contribution based on the Hebeker representation. For extreme conditions, such as drop-to-medium viscosity ratios significantly less than unity, it is found that upwind-biased methods are the only stable approaches for modeling surfactant transport. Two distinct schemes, upwind finite-volume and flow-biased least-squares, are found to provide results in close agreement, indicating negligible numerical diffusion. Surfactant transport is enhanced by low drop-to-medium viscosity ratios, at which extremely sharp concentration gradients form during various stages of the squeezing process. The presence of surfactant, even at low degrees of contamination, significantly decreases the critical capillary number for droplet trapping, due to the accumulation of surfactant at the downwind pole of the drop and its subsequent elongation. Increasing the degree of contamination significantly affects surface mobility and further decreases the critical capillary number as well as drop squeezing times, up to a threshold above which the addition of surfactant negligibly affects squeezing dynamics.

4.1 Surfactants are everywhere, and they greatly influence interfacial dynamics

Despite the prevalence of surfactants in confined biological and subsurface settings, their influence on fluid interfaces squeezing between solid boundaries remains largely uncharacterized. Surfactant-laden drop flow in the vicinity of solid obstacles gives rise to significant complexities due to the nonlinear coupling of interfacial hydrodynamics with surfactant transport and solid-phase contributions. A diverse set of fields
including biomicrofluidics, solid-phase catalysis and enhanced oil recovery may benefit from theoretical insight into this commonly-encountered but nontrivial system. Of fundamental interest is the ability to predict how the presence of surfactant affects drop transport through porous/granular media with respect to degree of contamination and fluid properties of the dispersed phase (Zinchenko & Davis, 2017b). To shed light on the influence of contamination on droplet flow near interstitial sites, a robust formulation for a surfactant-laden drop squeezing through a single interparticle constriction is developed in the present study.

There have been successful modeling efforts for each of the disparate components of the current system, namely (i) tight squeezing of clean drops and (ii) the effect of surfactant on fluid-phase emulsion flow without solid boundaries. Previous work has illuminated the critical role of lubrication forces between two approaching drops (Lee & Hodgson, 1968; Davis et al., 1989) or between a drop and a solid obstacle (Neitzel & Dell’Aversana, 2002; Barnocky & Davis, 1989). These forces allow a drop to closely approach a substrate without wetting the surface. In experimental studies, this separation has been cited as reducing to the level of a monolayer or a few layers of water molecules (Chen et al., 2018). Numerical Stokes flow solutions using idealized spherical obstacles also predict that tightly squeezing drops nearly coat solid particles, with drop-solid clearances several orders of magnitude smaller than droplet radii (Zinchenko & Davis, 2006). Therefore, modeling squeezing phenomena requires considerable robustness from numerical algorithms, which might be achieved with either interface capturing methods, such as that used by De Menech et al. (2008) for squeezing through microchannels, or desingularization techniques for formulations such as the boundary-integral method that specifically resolve the interface. A larger body of literature exists concerning the fundamental role of surfactants on fluid-fluid interfacial dynamics. One macroscale effect of surfactant is the reduction of surface tension. Contaminants also introduce an additional tangential stress along the interface due to gradients of surface tension, known as Marangoni stresses, which are responsible for interfacial stabilization or immobilization (Hosokawa et al., 2017). At high enough concentrations of certain surfactants, the surface can remobilize due to its inability to sustain the gradients necessary for Marangoni stresses (Stebe et al., 1991).

Much of the conventional wisdom regarding contaminated interface behavior involves one or more drops in pure fluid. The surface diffusivity of a typical surfactant is extremely weak, on the order of $10^{-6}$
cm² s⁻¹, and therefore much study has been devoted to non-diffusive surfactants (Eggleton et al., 1999). This assumption corresponds to the limit of large surface Péclet number $Pe \rightarrow \infty$, typical of highly-confined multiphase flows (Anna, 2016; Wrobel et al., 2018). Here, $Pe = U L / D_s$, where $U$ is a characteristic surface velocity (e.g., drop settling velocity or imposed interstitial flow velocity), $L$ is a characteristic length scale (e.g., drop diameter), and $D_s$ is surface diffusivity of surfactant. For example, using the above surface diffusivity, and a 1 mm droplet flowing through a packed bed with interstitial velocity 0.1 cm/s, a conservative estimate (see e.g. Lebon et al. (1996)), gives $Pe \sim 10^4$. The model of non-diffusive surfactant continues to apply even for a drop trapped in a constriction, with near-zero advancement velocity. In this case, the correct velocity scale in the Péclet number definition is a much larger tangential interface velocity (due to internal circulation); this velocity can be on the order of the single-phase flow field (see §4.5.2). In an imposed flow field such as extensional flow, surfactant tends to be swept in the direction of the flow and accumulate at drop poles. Surfactant localization can result in increased drop deformation, breakup or tip streaming, or a ‘stagnated cap’ as Marangoni stresses negate the developing surface stress field (Stone & Leal, 1990; Milliken et al., 1993; Kruijt-Stegeman et al., 2004). These phenomena tend to be enabled or enhanced by low drop-to-medium viscosity ratios (Eggleton et al., 1999).

Surfactants also influence the interaction of two or more drops by affecting the formation and draining of the lubrication layer, as has been investigated with respect to colliding drops (Yeo et al., 2003). Surfactant was concluded to retard the drainage of the lubrication layer due to interface immobilization. Interestingly, the viscosity ratio has a negligible effect on drainage dynamics when the film is immobilized (Klaseboer et al., 2000). Furthermore, it requires only a small amount of surfactant to achieve an immobilized interface (Lin & Slattery, 1982; Allan et al., 1961). Surfactant may also increase the deformability of dimples formed in the near-contact region, though it is not immediately obvious if this effect would accelerate or prolong lubrication layer draining (Chesters & Bazhlekov, 2000; Dai & Leal, 2008).

The inclusion of a spatially-fixed solid phase within a contaminated emulsion introduces a number of challenges, both in terms of physical modeling and accurate numerical treatment. Under tight squeezing conditions, a droplet may approach the solid surface to within a distance several orders of magnitude less
than the radius of the droplet (Bordoloi & Longmire, 2014). In the context of a boundary-integral formulation, this proximity necessitates higher-order desingularization techniques customized for the solid-phase contribution that account for both hydrodynamic (normal) and Marangoni (tangential) forces acting on the interface. Additionally, unlike isolated drops settling under gravity or subject to simple flows, complex patterns of surfactant may develop on the drop surface and be maintained at steady state, including the appearance of sharp concentration gradients. With respect to a numerical implementation, it was found in the present work that a stable algorithm for surfactant convection, particularly at low drop-to-medium viscosity ratios and negligible diffusion, requires the use of an upwind-biased scheme. Finally, it is not immediately obvious how lubrication forces between a solid particle and a deformable drop will be affected after contaminating the drop. The coupling between these physical considerations make it difficult to intuit the extent to which surfactant should increase or decrease squeezing times, assumed to be dependent on the competing effects of locally increased surface deformability and immobilization of the drop interface. Therefore, a fully three-dimensional model that explicitly resolves the interface is necessary for investigating contaminated drop squeezing.

The technical aspect of modeling surfactant contributions largely revolves around accurately capturing interface phenomena and has been achieved with space-filling gridded techniques, such as front tracking (de Jesus et al., 2015), embedded boundary (Khatri & Tornberg, 2014), level-set (Xu et al., 2012) or phase-field (Liu & Zhang, 2010) and lattice Boltzmann (Riaud et al., 2018) methods. These efforts have primarily focused on drops subject to an imposed shear, extensional, or channel flow. For example, Park et al. (2013) discussed the effect of surfactant on droplet formation through a flow-focusing device using a diffuse-interface method, suggesting that the drop radii decreases with increasing surfactant coverage. Riaud et al. (2018) elucidated the conditions under which stagnant caps can form on drops flowing through a T-junction microchannel, and that surfactant can reduce drop squeezing time in this situation. Farhat et al. (2011) showed that droplet elongation increases with surfactant coverage in simple shear and extensional flows, using a lattice Boltzmann approach. Using a similar method, Liu & Zhang (2010) demonstrated that surfactants inhibit coalescence by reducing interface mobility and slowing film drainage. Finally, boundary-integral methods can be used to selectively solve for interfacial behavior with respect to
various equations of state (Li & Pozrikidis, 1997; Eggleton et al., 1999) as well as large degrees of drop deformation and breakup (Bazhlekov et al., 2006), using schemes of arbitrary order of accuracy.

Extending the goals of prior work by Zinchenko & Davis (2006) on clean drops, we study herein how the surface contamination of a drop with insoluble surfactant affects its flow-induced squeezing through a constriction between several solid particles in the Stokes regime. To effect tight-squeezing conditions, the non-deformed drop diameter is larger than the constriction diameter. An immediate goal is to probe the effects of the surfactant surface coverage, capillary number and viscosity ratio on the squeezing time, surfactant distribution and critical conditions for drop trapping. Even more important for the research community, this small-scale, but still challenging 3D problem serves as a prototype for drop squeezing through a granular medium (with relevance, e.g., to oil recovery). Robust simulation tools developed herein for surfactant transport will be indispensable in future multipole-accelerated, multidrop-multiparticle simulations for emulsion flow through a packed bed; as an example, boundary-integral desingularization tools from Zinchenko & Davis (2006) were essential in large-scale simulations of Zinchenko & Davis (2013) for clean drops.

The problem formulation, relevant parameters and simulation setup are discussed in §4.2. An overview of the boundary-integral equations is provided in §4.3. Comprehensive analysis of various schemes for transport of non-diffusive surfactant on a deformable surface is given in §4.4. The finite-volume algorithm (Bazhlekov et al., 2003) used for a single drop in shear flow, and the least-squares method of Zinchenko & Davis (2017a) for concentrated emulsions, turn out to be very restrictive in tight squeezing simulations, not allowing, in particular, for small viscosity ratios. The difficulties with both methods (namely, surface tension becoming negative) in the zero-diffusion limit were puzzling and unresolved in prior work; physical deficiency of the linear equation of state for surfactant was even suspect (Zinchenko & Davis, 2017a; Bazhlekov et al., 2006). We show here instead that the issue of negative surface tension arises from numerical instability and is eliminated by a flow-biased surfactant transport scheme. Two competitive stable schemes are offered in §4.4, namely, an upwind finite-volume version for a deformable surface (more in line with traditional upwind algorithms in inviscid flow modeling, e.g. Smolarkiewicz & Szmelter (2005)), and a substantially new flow-biased least-squares method. Close agreement between the
results by these two, very distinct methods is the evidence that numerical diffusion (inherent in both methods) does not come into play appreciably in the range of parameters and resolutions of the present study. Convergent tight squeezing simulations always require extreme resolutions anyway, both for drop and solid surfaces, even with the present boundary-integral algorithm that explicitly resolves the boundaries. So, it seems problematic to reach similar goals with alternative approaches using space-filling grids (e.g. with the volume of fluid (VOF) method). In §§4.5-4.6, we summarize major trends observed for contaminated drop squeezing, with particular focus on the influence of surfactant on critical capillary number and interfacial behavior under a wide range of viscosity ratios.

4.2 A model problem for surfactant-covered droplet flows

Consider a single deformable drop freely-suspended in a uniform far-field flow, covered with an initially uniform insoluble surfactant and approaching an array of spatially-fixed solid particles, where both liquid phases are described by Stokes flow and assumed Newtonian. A constriction is formed by three equi-sized solid spheres arranged in an equilateral triangle (as in figure 4.1a, for a resolution of \( N_\Delta = 8640 \) mesh triangles per particle). In what follows, \( \tilde{N}_\Delta \) and \( \tilde{N}_\tilde{\Delta} \) will refer to solid-particle and drop mesh resolutions, respectively, and the abbreviations 8.6K, 11.5K, 15.4K, 20K and 46K will be used for \( N_\Delta = 8640, 11520, 15360, 20480 \) and 46080. Defining the characteristic length \( L \) of the system as the radius of a solid particle, the drop centre is initially placed \( 6L \) upstream of the particles’ basal plane, unless otherwise noted. The ratio between undeformed drop and solid radii, \( \tilde{a}/L \), is fixed at 0.6, and the interparticle gap (\( \epsilon \)) is fixed at 0.25\( L \), for all simulations herein. The ratio of the drop viscosity (\( \mu_d \)) and medium viscosity (\( \mu_e \)) is \( \lambda = \mu_d/\mu_e \), and the uniform far-field velocity carrying the drop towards the constriction is \( u_\infty \) (figure 4.1b).

Surfactant-concentration (\( \Gamma \), in moles/area) and surface-tension (\( \sigma \)) gradients develop from their uniform distribution on the drop as it nears the constriction. An important metric of drop squeezing behavior is the drop squeezing time \( T_s \). For the purposes of this study, a drop is defined to be in a squeezing state if its instantaneous centre-of-mass velocity \( U \) (see below) is less than 1\% of the uniform far-field velocity \( |u_\infty| \).
The non-dimensional elasticity parameter $\beta$, a measure of the degree of surface contamination, is defined as

$$
\beta = \Gamma_{eq} \frac{RT}{\sigma_o} = \frac{Q}{4\pi \tilde{a}^2} \frac{RT}{\sigma_o}, \quad \text{where} \quad Q = \int_{\tilde{S}} \Gamma dS,
$$

(4.1)

$\sigma_o$ signifies clean-drop surface tension, $\tilde{S}$ represents the drop surface, and equilibrium (eq) is defined as the case of uniform surfactant concentration on a spherical drop. We assume a linear equation of state

$$
\sigma = \sigma_o - RT \Gamma,
$$

where $R$ is the universal gas constant and $T$ the uniform absolute temperature. The equilibrium surface tension can then be expressed as

$$
\sigma_{eq} = \sigma_o (1 - \beta).
$$

(4.2)

The capillary number is defined using the equilibrium surface tension:

$$
Ca = \frac{\mu_{\infty} |u_{\infty}| \tilde{a}}{\sigma_{eq} L}.
$$

(4.3)

Several other metrics are used to quantify squeezing behavior. The gap between the drop and each solid particle is defined as the minimum distance between the drop mesh polyhedron, assuming flat triangulation, and the particle centre minus the particle radius. The instantaneous drop velocity $U$, defined as the volume-averaged fluid velocity $u$ inside the drop, can be calculated through the divergence theorem as

$$
U = \langle u \rangle = \frac{1}{V} \int_{\tilde{S}} (\mathbf{u} \cdot \mathbf{n})(\mathbf{x} - \tilde{x}^c) \, dS,
$$

(4.4)

where $V$ is the drop volume, $\mathbf{n}$ are outward surface unit normals at points $\mathbf{x}$ on the surface, and $\tilde{x}^c$ is the drop centroid. In what follows, $U$ is the component of $\mathbf{U}$ along $u_\infty$.

The simplest equation of state $\sigma = \sigma_o - RT \Gamma$ used herein (and elsewhere) is the linearization of the Langmuir-Szyszkowski equation $\sigma = \sigma_o + RT \Gamma \ln(1 - \Gamma/\Gamma_\infty)$ for $\Gamma \ll \Gamma_\infty$, where $\Gamma_\infty$ is the maximum surfactant concentration for complete surface coverage as a monolayer; accordingly, $\Gamma_\infty$ falls out from the formulation. In our simulations, the surface average $<\Gamma>$ remains close to $\Gamma_{eq}$, due to surfactant conservation and modest changes in the drop surface area, even for significant deformations. For this
reason, $\Gamma_{eq} \ll \Gamma_{\infty}$ (rather than $\Gamma \ll \Gamma_{\infty}$) is believed to be an appropriate condition for linearization of $\sigma(\Gamma)$ to not appreciably affect the global squeezing dynamics; incidentally, in our stable simulations with linear $\sigma(\Gamma)$, Marangoni stresses do not allow $\Gamma$ to greatly exceed $\Gamma_{eq}$ (thus keeping $\sigma$ positive). The condition $\Gamma_{eq} \ll \Gamma_{\infty}$ translates into $\beta \ll E$, with $E = RT\Gamma_{\infty}/\sigma_0$. From experimental data for several surfactants, Eggleton et al. (1999) report the values of $E \sim 0.15 - 0.5$, although there are no theoretical arguments why they can not be higher. For $E \sim 0.3 - 0.5$, the condition $\beta \ll E$ is roughly met for most of our simulations.

### 4.3 Boundary-integral formulation for contaminated drops

The present boundary-integral formulation for contaminated drop squeezing combines the approaches previously developed for interparticle squeezing of clean drops (Zinchenko & Davis, 2006) and free-space flows of contaminated emulsions (Zinchenko & Davis, 2017a). The Hebeker representation for solid-particle contributions is used along with custom, high-order desingularization techniques for drop-solid, solid-solid and self-interactions, in order to treat tight squeezing conditions. The appearance of Marangoni stresses due to surfactant gradients results in an additional tangential component of the stress jump at the drop interface. The components of the interfacial stress are individually desingularized for both drop
self-interactions and drop-solid contributions. The formulation results in well-behaved Fredholm integral
equations of the second kind and allows accurate modeling of near-critical conditions, for which drop-solid
separation distances can be several orders of magnitude smaller than the drop radius.

Let \( \tilde{N} \) be, for generality, the number of drops in the system, \( \tilde{S} \) be the surfaces of these drops, \( \hat{N} \) be
the number of solid particles and \( \hat{S} \) be the surfaces of these particles. The no-slip boundary condition
\( \mathbf{u} = 0 \) is enforced for the fluid velocity on the solid boundaries. The far-field velocity \( \mathbf{u}_\infty(y) \) away from the
particles and drops can be an arbitrary Stokes flow (although a uniform \( \mathbf{u}_\infty \) was assumed in the present
simulations). Standard Wielandt’s deflation is used to avoid ill-conditioning at the low viscosity ratios of
interest for this study. To this end, the system is cast in terms of \( \mathbf{w} = \mathbf{u} - \kappa \mathbf{u}' \), where \( \kappa = (\lambda - 1)/(\lambda + 1) \)
and \( \mathbf{u}' \) is the rigid-body projection of \( \mathbf{u} \). At every time step, the following system of equations is solved for
modified interface velocity \( \mathbf{w} \) on drops and Hebeker density \( \mathbf{q} \) on solid surfaces:

\[
\mathbf{w}(y) = \frac{2F(y)}{\lambda + 1} + \kappa \left[ \frac{2}{\lambda + 1} \sum_{\beta=1}^{\tilde{N}} \int_{\tilde{S}_\beta} \mathbf{w}(x) \cdot \mathbf{\tau}(r) \cdot \mathbf{n}(x) dS_x - \mathbf{w}'(y) + \frac{n(y)}{S_\alpha} \int_{\tilde{S}_\alpha} \mathbf{w} \cdot \mathbf{n} dS \right] \\
+ \frac{2}{\lambda + 1} \sum_{\beta=1}^{\hat{N}} \int_{\hat{S}_\beta} \mathbf{q}(x) \cdot [2\mathbf{\tau}(r) \cdot \mathbf{n}(x) + \eta \mathbf{G}(r)] dS_x 
\tag{4.5}
\]

for \( y \in \tilde{S}_\alpha \) and

\[
\mathbf{q}(y) = F(y) + (\lambda - 1) \sum_{\beta=1}^{\tilde{N}} \int_{\tilde{S}_\beta} \mathbf{w}(x) \cdot \mathbf{\tau}(r) \cdot \mathbf{n}(x) dS_x \\
+ \sum_{\beta=1}^{\hat{N}} \int_{\hat{S}_\beta} \mathbf{q}(x) \cdot [2\mathbf{\tau}(r) \cdot \mathbf{n}(x) + \eta \mathbf{G}(r)] dS_x 
\tag{4.6}
\]

on solid-particle surfaces (\( y \in \hat{S}_\alpha \)), where \( \mathbf{r} = \mathbf{x} - y \), \( \mathbf{n} \) is the unit normal to the surface, \( \eta > 0 \) is the
Hebeker parameter (the choice of \( \eta \) affects the algorithm robustness, but not the solution upon numerical
convergence), and prime indicates rigid-body projection. The single-layer terms containing the Hebeker
parameter \( \eta \) serve to complete the range of boundary-integral operators; without these terms, the
double-layer boundary-integral contribution could not accommodate non-zero forces or torques acting on
the solid particles. Here, and for the remainder of §4.3, the index \( \beta \) should not be confused with the
elasticity parameter. To account for Marangoni stresses, the boundary-integral equations are modified from Zinchenko & Davis (2006) in the definition of $F(y)$, as:

$$F(y) = u_\infty(y) + \sum_{\beta=1}^{N} \int_{\bar{S}_\beta} f(x) \cdot G(x - y) \, dS_x$$

(4.7)

with

$$f(x) = \frac{1}{\mu_e} (2\sigma(x)k(x)n(x) - \nabla_s \sigma) \quad (x \in \bar{S}_\beta),$$

(4.8)

where $\nabla_s$ is the surface gradient and $k$ is the mean surface curvature $k(x) = (k_1 + k_2)/2$, with $k_1$, $k_2$ being the principal curvatures at $x$. Finally, $G(r)$ and $\tau(r)$ are the free-space Green tensor and the corresponding fundamental stresslet, respectively:

$$G(r) = -\frac{1}{8\pi} \left[ \frac{I}{r} + \frac{rr}{r^3} \right], \quad \tau(r) = \frac{3}{4\pi} \frac{rrr}{r^5}.$$  

(4.9)

After desingularization of droplet-droplet, droplet-particle, and particle-particle interactions, equations (4.5)-(4.6) can be solved by GMRES iterations, and node positions can be time-integrated using a second or first-order Runge-Kutta scheme. An improved surface integration scheme, which treats the mesh triangles on spherical solid particles as curved geodesic triangles, allows for better convergence with respect to surface triangulation in drop squeezing simulations (see Zinchenko & Davis, 2013). Mesh quality is maintained using passive mesh stabilization, as in Zinchenko & Davis (2006).

Single-layer desingularization in (4.7) for an arbitrary vector field $f(x) = f_\parallel(x) + f_n(x)n(x)$, where $f_\parallel$ is the tangential component and $f_n = f \cdot n$ is the normal component, is achieved with the general relation

$$\int_S f(x) \cdot G(x - y) \, dS_x = \int_S [f - (n \cdot n^*)f_\parallel^* - (f_\parallel^* \cdot n)n^* - f_n^*n] \cdot G(x - y) \, dS_x$$

$$+ \int_S [(x - x^*) \cdot n^*]f_\parallel^* \cdot \tau(x - y) \cdot n \, dS_x.$$

(4.10)
Here, $y$ may be an observation point either on or outside $S$. If $y \in S$ then $x^* = y$, otherwise $x^* \in S$ is chosen as the mesh node on $S$ nearest to $y$. The superscript $^*$ denotes values at $x^*$, and $f = f(x)$ and $n = n(x)$ on the right-hand side for conciseness. Further technical details regarding these techniques have been discussed at length by Zinchenko & Davis (2006, 2017a).

### 4.4 Surfactant transport and numerical considerations for BIM

Surface diffusion of a typical surfactant is weak, and transport is dominated by surface convection in many cases of practical interest (see §1). When neglecting diffusion, the transport of local surfactant concentration is solely due to convection and Marangoni stresses on the deformable the drop surface. The problem therefore reduces to the pure convection of a nonnegative scalar field confined to a closed, deformable surface. For tight-squeezing contaminated drops, a characteristic aspect of the surfactant distribution is the development of sharp concentration gradients, due to the interaction between Marangoni stresses and squeezing drop hydrodynamics. Several formulations were implemented in the present work in an attempt to achieve universal stability while adequately resolving these gradients. Simulations at high viscosity ratio ($\lambda = 4$) were completed using the least-squares scheme with small, variable artificial diffusion (with the goal of achieving the zero-diffusion limit globally) presented in detail by Zinchenko & Davis (2017a), but this method was found to develop numerical instabilities at low drop-to-medium viscosity ratios. An alternative discussed therein, namely utilizing a simple conservation law for purely non-diffusive surfactant, was also tested extensively but simulations crashed at similar times, due to numerical oscillations resulting in local areas of unphysically high surfactant concentrations. The non-diffusive, finite-volume formulation for unstructured surface meshes presented by Bazhlekov et al. (2003) was explored in the present work with options for explicit, semi-implicit and implicit time integration, and was found to significantly increase stability but was unable to continue simulations to drop exit, also due to oscillatory behavior at low viscosity ratios. Instead, a first-order upwind finite-volume scheme was found to stably model surfactant transport while still resolving the surfactant distribution without diffusion. Finally, a flow-biased least-squares scheme (without diffusion) was developed, which also
decreases the order of surfactant-gradient fitting but retains higher-order velocity paraboloid fitting for each node. Results as well as convergence behavior obtained using this latest scheme were found to agree with those by the upwind finite-volume scheme.

A consideration common to all implementations is accounting for nodal velocity $V = u + w$ not being equal to interfacial velocity $u$, due to the use of passive mesh stabilization to maintain mesh quality. We begin with the dimensional convection-diffusion equation for a deformable surface,

$$\frac{d\Gamma}{dt} = w \cdot \nabla_s \Gamma - \Gamma \nabla_s \cdot u - 2k \Gamma u \cdot n + D_s \nabla^2_s \Gamma,$$

(4.11)

where $d/dt$ is the time derivative for a node moving with velocity $V$, $u$ is the interfacial fluid velocity, $k$ is the local mean curvature, $n$ is the drop surface outward normal, $D_s$ is the surfactant diffusivity (set to zero when neglected, see below), and $\nabla_s$ is the surface gradient operator (by definition, only the tangential component $u_s$ of $u$ participates in the divergence operation $\nabla_s \cdot u$). Also, in all implementations, surfactant concentration is rescaled at every time step to preserve the total amount of surfactant over long simulation times (even though, at each time step, the rescaling factor is extremely close to unity and approaches this limit for high resolutions).

### 4.4.1 Least-Squares Scheme

The least-squares (LS) scheme detailed in Zinchenko & Davis (2017a) utilizes rigorously-derived high-order approximations for the surface metric tensor and relevant per-node properties. The physical drop surface is locally parameterized in curvilinear coordinates by a paraboloid, and nodal velocity, surfactant concentration and other physical quantities are found by a least-squares quadratic fitting with first-level neighbouring nodes. Numerical instabilities are smoothed by introducing a tunable, small artificial surfactant diffusivity ($D_s$). Accordingly, the transport equation is generalized to

$$\frac{d\Gamma}{dt} = (w + \nabla_s D_s) \cdot \nabla_s \Gamma - \Gamma \nabla_s \cdot u - 2k \Gamma u \cdot n + D_s \nabla^2_s \Gamma,$$

(4.12)
where

\[
D_s = \eta \frac{(\sigma_{eq})^2 \tilde{a}}{\mu_c \sigma} \tag{4.13}
\]

and \( \eta \) is a small, non-dimensional parameter (not to be confused with the Hebeker parameter in §4.3). As compared to the pure two-fluid systems (without solid boundaries) studied by Zinchenko & Davis (2017a), it was found in the present work that drop tight-squeezing dynamics are more sensitive to \( \eta \). For \( Ca = 0.9 \), \( \lambda = 1.0 \), and \( \beta = 0.05 \), a threefold decrease in this value resulted in unstable simulations, while a threefold increase resulted in significantly altered squeezing times. A value \( \eta = 1.9 \times 10^{-4} \), empirically optimized for highly concentrated emulsions (Zinchenko & Davis, 2017a), was found in the present study to be near the minimum value that alleviates instabilities at non-critical capillary numbers while reproducing the dynamics of exactly non-diffusive algorithms.

At low viscosity ratios, LS was not found to be a stable scheme to model surfactant transport. Stability was not significantly improved by decreasing the time step or increasing mesh resolutions. Decreasing the time step threefold and increasing mesh resolution twofold (\( \tilde{N}_\Delta = 46K, \hat{N}_\Delta = 20K \)), while also being prohibitively expensive in terms of run time, resulted in the familiar unphysical accumulation of surfactant in one or more nodes. During these ultra-high accuracy attempts, the numerical instability occurred consistently at the ‘triple-point’ of surfactant distribution above solid-particle interstices, a characteristic concentration profile visualized in §4.5. Increasing the artificial diffusion parameter \( \eta \) in these cases, while potentially resulting in a stable simulation, would mask sharp gradients and result in greater diffusion of surfactant into near-contact regions.

### 4.4.2 Finite-Volume (FV) Scheme

The integral form of (4.11) results in a finite-volume formulation of surfactant transport. In this formulation, the surfactant concentration at each node is updated using the sum of concentration fluxes through the faces of the dual mesh. A typical dual cell is illustrated in figure 4.2. The contour \( C_i \) of the dual-mesh cell \( S_i \) around node \( \mathbf{x}_i \) of the triangle mesh is formed by the edge midpoints of triangles sharing
Figure 4.2: A typical dual-mesh cell $S_i$ (shaded gray) used for finite-volume formulations of surfactant transport. Surfactant flux through cell edges determines the change in concentration at a node $x_i$, influenced by neighbouring nodes $x_j$. The dual-cell contour is defined by edge midpoints and triangle centroids. A contour segment has length $l_k$, and its unit normal $b_k$ is in the plane of its containing triangle.

node $x_i$ and triangle centroids, as shown in figure 4.2. As introduced by Yon & Pozrikidis (1998), after neglecting diffusion, this refactoring results in the balance

$$\int_{S_i} \frac{d\Gamma}{dt} dS = \int_{S_i} (w + \mathbf{u}) \cdot \nabla_s \Gamma \ dS - \int_{S_i} \nabla_s \cdot (\Gamma \mathbf{u}) \ dS - 2 \int_{S_i} \Gamma \mathbf{u} \cdot \mathbf{n} \ dS.$$  \hspace{1cm} (4.14)

Converting (4.14) into numerical form, as provided by Bazhlekov et al. (2003), results in the following discrete terms:

$$\int_{S_i} (w + \mathbf{u}) \cdot \nabla_s \Gamma \ dS \approx \frac{1}{3} (w + \mathbf{u})_i \cdot \sum_{j \in N^T_i} \left( \nabla_s \Gamma \right)_j A_j,$$  \hspace{1cm} (4.15)

where the subscript $i$ denotes values at node $i$, $N^T_i$ is the set of triangles containing node $i$, $A_j$ is the area of the $j^{th}$ triangle, and $\Gamma$ in each triangle is a linear interpolation of the nodal values,

$$\int_{S_i} \nabla_s \cdot (\Gamma \mathbf{u}) \ dS = \int_{C_i} \Gamma \mathbf{u} \cdot \mathbf{b} \ dC \approx \sum_k \left( b_k \cdot \int_{L_k} \Gamma \mathbf{u} \ dl \right),$$  \hspace{1cm} (4.16)
where the summation is over all straight contour segments $L_k$ in $C_i$ (two per mesh triangle), $b_k$ is the outward unit normal to segment $L_k$ of length $l_k$ (see figure 4.2), values at contour segment endpoints are determined from a linear interpolation within their containing mesh triangle, the integral on the right-hand side of (4.16) is calculated using the trapezoid rule, and

$$\int_{S_i} \Gamma k u \cdot n \, dS \approx \Gamma_i k_i (u_i \cdot n_i) S_i,$$  (4.17)

with the dual-cell area

$$S_i = \frac{1}{3} \sum_{j \in N_i^T} A_j.$$  (4.18)

The numerical form of the convection equation can be written as a system of equations

$$\frac{d\Gamma_i}{dt} = \sum_{j \in (N_i \cup i)} A_{ij} \Gamma_j, \quad i = 1, 2, \ldots, N,$$  (4.19)

where $A_{ij}$ coefficients are a function of given node positions and velocities, $N_i$ is the set of neighbouring mesh nodes (see figure 4.2), and $N$ is the total number of drop mesh nodes. It is straightforward to study various time integration methods for (4.19) via the theta method,

$$\Gamma_i(t + \Delta t) = \Gamma_i(t) + \Delta t \sum_{j \in (N_i \cup i)} A_{ij} \cdot [\theta \Gamma_j(t + \Delta t) + (1 - \theta) \Gamma_j(t)],$$  (4.20)

where $\theta = 0$ corresponds to Euler explicit time integration, $\theta = 0.5$ to Crank-Nicholson, and $\theta = 1$ to fully implicit. The Gauss-Seidel iteration was used to solve the system of equations when necessary.

The FV implementation tested here differs from that of Bazhlekov et al. (2003) in the calculation of mean curvature and surface normals. Rather than via contour integration, curvature and normal vectors are obtained by best paraboloid fitting (Zinchenko et al., 1997). This method exploits the observation that a smooth interface may be locally approximated by quadratic surface. This distinction in methodology is important due to the large deformations experienced by a drop during tight squeezing, which result in
significant deviation from its initial sphericity, including transient nearly-flat areas. As noted by Zinchenko et al. (1997), mean curvature calculation via paraboloid fitting eliminates difficulties inherent in the contour integration method and demonstrates superior convergence in the nearly-flat and near-contact dimple regions that play a critical role in lubrication.

The primary objective of exploring alternate transport schemes is to stably treat low drop-to-medium viscosity ratios while sharply resolving regions of high gradient. Therefore, no attempt was made in the present work to incorporate artificial diffusion into the FV scheme. Instead, several types of time integration were investigated using high mesh resolutions ($\tilde{N}_\Delta = 20K$). Overall, this non-diffusive FV scheme was found to notably improve numerical stability near critical conditions. For example, simulations failed after a short time at $Ca = 0.9$, $\lambda = 0.25$, and $\beta = 0.05$ when using the LS scheme (even with implicit time integration), but the FV version proceeded past the global minimum drop velocity before suffering from similar instabilities and mesh degradation near sharp concentration gradients. However, spurious oscillations in the surfactant concentration occasionally appeared during the onset of squeezing, usually immediately upwind from developing sharp gradients. These unphysical numerical artifacts were not eliminated by semi-implicit (Crank-Nicholson) or fully implicit time integration. Away from critical parameters, erroneous oscillations are minimal and the FV scheme proves to be a reliably stable method for purely non-diffusive surfactant transport.

### 4.4.3 Upwind FV Scheme

Convection-dominated transport of compressible media can be modeled by a formulation biased toward the upwind contribution of the velocity field. Upwind schemes generally increase the stability of convected scalar fields that may contain sharp gradients, at the cost of introducing numerical diffusion that is dependent on mesh resolution. For an upwind version of the FV surfactant transport algorithm, we follow the ideas of first-order schemes from inviscid fluid modeling (Smolarkiewicz & Szmelter, 2005). In the present context, it is advantageous first to reformulate the non-diffusive form of the transport equation (4.11) for node $i$ using the reference frame translating with the nodal velocity $V_i$, and the corresponding relative fluid velocity $u - V_i$ near node $i$. From the relation $\nabla_s \cdot C = -2kC \cdot n$ valid for any constant
vector $C$ on a surface, eqn. (4.11) can be formally rewritten as

$$\frac{d\Gamma}{dt} = w \cdot \nabla_s \Gamma - \nabla_s \cdot [\Gamma(u - V_i)] + (u - V_i) \cdot \nabla_s \Gamma + 2k\Gamma(V_i - u) \cdot n \quad (4.21)$$

at node $i$ (on the understanding that $V_i$ is treated as constant in the differential operation of eqn. (4.21)). The last term in (4.21) vanishes, since the nodal velocity $V_i = dx_i/dt$ is constructed to always have the same normal component as the fluid velocity $u$ for correct drop shape evolution. Recollecting the definition $V = u + \omega$ brings (4.21) to the simple form

$$\frac{d\Gamma}{dt} = -\nabla_s \cdot (\Gamma(u - V_i)) \quad (4.22)$$

at node $i$. Using eqn. (4.22) not only eliminates the need for curvature calculation (which could be unsatisfactory with some methods), but was also found in the present work to improve stability of the surfactant transport scheme.

Based on the integral form of (4.22), the surfactant concentration at node $i$ is updated as

$$\Gamma_i^{n+1} = \Gamma_i^n - \frac{\Delta t}{S_i} \sum_k F_k^\perp l_k, \quad (4.23)$$

where the summation is, again, over all straight contour segments $L_k$ with length $l_k$, and $F_k^\perp$ is the normal flux of $\Gamma$ through $L_k$ per unit length. Let $(x_i + x_j)/2$ be the mesh edge midpoint associated with $L_k$ (figure 4.2), and

$$v^\perp = \left[\frac{1}{2}(u_i + u_j) - V_i\right] \cdot b_k \quad (4.24)$$

be the approximation for the relative velocity component $(u - V_i) \cdot b_k$ on $L_k$. Following the pattern of upwind schemes, the flux calculation depends on the sign of $v^\perp$:

$$F_k^\perp = [v^\perp]^+ \Gamma_i^n + [v^\perp]^- \Gamma_j^n, \quad (4.25)$$
where, in general,

\[
[v]^+ \equiv 0.5(v+|v|), \quad [v]^− \equiv 0.5(v−|v|).
\]  \hspace{1cm} (4.26)

Many advanced upwind schemes have been developed for inviscid fluid modeling in order to treat high Reynolds numbers compressible flows, which may contain large density gradients or time-dependent shock waves. In the present quasi-steady-state regime, it is unlikely that higher-order schemes will significantly increase the accuracy with respect to drop squeezing dynamics. The above first-order upwind FV scheme for unstructured meshes was found to be in close agreement with both LS and strictly conservative FV formulations at moderately high viscosity ratios, even near critical squeezing conditions (see figure 4.3 and §4.5). It is therefore used to predict the squeezing behavior at more extreme viscosity ratios that previous implementations are unable to model. Euler explicit time integration was used for all upwind FV simulations.
4.4.4 Flow-Biased Least-Squares (FBLS) Scheme

We have found most recently that the stability of the simple least-squares method of Zinchenko & Davis (2017a) for the transport equation (4.11) can be also greatly increased by reducing the order of approximation for \( \mathbf{w} \cdot \nabla_s \Gamma \) (the convective term primarily responsible for stability), instead of introducing artificial diffusion \( D_s \). In the intrinsic coordinate system \((x'_1, x'_2, x'_3)\) centred at node \( O \), with the \( x'_3\)-axis along the normal vector \( \mathbf{n}_O \) (here and below, subscript \( O \) relates to quantities at node \( O \)), the surface can be approximated as a paraboloid \( x'_3 = C(x'_1)^2 + D x'_1 x'_2 + E(x'_2)^2 \) near \( O \), which gives local parameterization in terms of \( x'_1 \) and \( x'_2 \). As in Zinchenko & Davis (2017a), quadratic polynomials are used to approximate the first two intrinsic fluid velocity components \( u'_\alpha \) (\( \alpha = 1, 2 \)) near \( O \):

\[
u'_\alpha(x'_1, x'_2) = (u'_\alpha)_O + a_\alpha x'_1 + b_\alpha x'_2 + c_\alpha (x'_1)^2 + d_\alpha x'_1 x'_2 + e_\alpha (x'_2)^2.
\]  

(4.27)

The five coefficients \( a_\alpha \ldots e_\alpha \) are found by least-squares fitting of (4.27) to the values of \( u'_\alpha \) for the whole set \( A \) of mesh nodes \( x_j \) directly connected to \( O \). This fitting is well-defined, since the coordination number of any node \( O \) for our meshes is at least five (typically six). The divergence and curvature terms in (4.11) combine to (Zinchenko & Davis, 2017a)

\[-\Gamma_O (\nabla_s \cdot \mathbf{u} + 2 k \mathbf{u} \cdot \mathbf{n})_O = -\Gamma_O (a_1 + b_2), \]

(4.28)

so this method, again, does not require curvature calculation.

For surfactant concentration, in contrast, a local linear approximation is used,

\[
\Gamma(x'_1, x'_2) = \Gamma_O + A x'_1 + B x'_2,
\]

(4.29)

with coefficients \( A \) and \( B \) required to provide the least-squares fit of (4.29) to \( \Gamma \)-values in the selected
subset (see below) \( A_{sel} \subset A \) of mesh nodes around \( O \):

\[
\sum_{j \in A_{sel}} \left[ A(x_j')_1 + B(x_j')_2 - \Delta \Gamma_j \right]^2 \rightarrow \min, \quad \Delta \Gamma_j = \Gamma(x_j) - \Gamma_O.
\] (4.30)

The fitting operation (4.29)-(4.30) requires \( A_{sel} \) to include at least two neighbours. Let the excess velocity \( w_O \) be \((w'_1, w'_2, 0)\) in the intrinsic basis. Solving (4.30) for \( A \) and \( B \), the convection term can be written as

\[
(w \cdot \nabla_s \Gamma)_O = \sum_{j \in A_{sel}} \mu_j \Delta \Gamma_j,
\] (4.31)

with the coefficients

\[
\mu_j = \frac{w'_1 [(x_j')_1 T_{22} - (x_j')_2 T_{12}] + w'_2 [T_{11}(x_j')_2 - T_{12}(x_j')_1]}{T_{11} T_{22} - T_{12}^2}
\] (4.32)

and

\[
T_{\alpha\beta} = \sum_{j \in A_{sel}} (x_j')_\alpha (x_j')_\beta.
\] (4.33)

A standard, rigorously-derived stability requirement for surfactant update

\[
\Gamma_O^{n+1} = \Gamma_O^n + \Delta t \sum_{j \in A_{sel}} \mu_j (\Gamma_j^n - \Gamma_O^n) + ...
\] (4.34)

is \( \mu_j > 0 \) for all \( j \in A_{sel} \) (at sufficiently small \( \Delta t \)). Accordingly, to construct \( A_{sel} \), we start from all neighbours (\( A_{sel} = A \)), calculate \( \mu_j \) from (4.32)-(4.33) and exclude the neighbour \( j \) with the most negative \( \mu_j \). The calculations (4.32)-(4.33) are then repeated, if necessary, for the reduced set \( A_{sel} \) to find and exclude another neighbour \( j \) with the most negative \( \mu_j \), etc., until the set \( A_{sel} \) is achieved with all positive \( \mu_j \). This logic can sometimes reduce \( A_{sel} \) to two neighbours, with one \( \mu_j \) still negative; in this case, node selection is forcefully terminated at two neighbours left to calculate the convective term, notwithstanding
µ_j < 0. Such events were extremely rare in our simulations and did not jeopardize stability. On average, the set \( A_{sel} \) is observed to contain three neighbours. Also note that \( \mu_j > 0 \) is not the same as the intuitive upwind condition \( w'_1(x'_j)_1 + w'_2(x'_j)_2 > 0 \). The FBLS method is quite simple in terms of programming and agrees well with all tested convection schemes at high viscosity ratio near critical conditions (figure 4.3).

Moreover, this scheme is stable at all parameter sets of interest and was used to complement, and as an additional validation of, the upwind FV method; at low viscosity ratios (\( Ca = 1.1, \lambda = 0.1, \beta = 0.05 \)), squeezing times agree to within \(~2\%\) at resolutions of \( \tilde{N}_\Delta = 15.4K \) and \( \tilde{N}_\Delta = 11.5K \) (see \S 4.5.3 for more comparisons).

### 4.5 A contaminated drop squeezing between spheres: simulation results

All values from the numerical simulations of contaminated drop tight squeezing are reported in non-dimensional form. The characteristic length scale \( L \) is taken as the solid-particle radius \( \hat{a} \). The velocity and times scales are \( |u_\infty| \) and \( L/|u_\infty| \), respectively. Surface tension and surfactant concentration at the drop surface are scaled with their equilibrium values, where equilibrium (\( eq \)) is defined as the case of uniform surfactant concentration on a spherical drop:

\[
\Gamma^* = \Gamma / \Gamma_{eq}, \quad \sigma^* = \sigma / \sigma_{eq}.
\] (4.35)

For the entirety of this section, the superscript * will be dropped for conciseness. The Hebeker parameter \( \eta \) in the boundary-integral formulation (equations 4.6-4.5) is set to unity. The initial drop shape is spherical, far upstream from the constriction and covered in uniformly-distributed surfactant. Definitions of \( Ca, \lambda, \) and \( \beta \) are provided in \S 4.2.
4.5.1 Numerical convergence tests

Most simulations were completed with high mesh resolutions (\(\tilde{N}_\Delta: 15.4K-20K, \tilde{N}_\Delta: 11.5K-20K\)) for accurate drop-squeezing simulations. The effect of drop triangulation with the LS method for surfactant transport is shown in figure 4.4. Away from critical conditions there is a negligible dependence of squeezing dynamics on drop mesh resolution for \(\tilde{N}_\Delta \geq 11.5K\). Closer to critical \(Ca (Ca_{crit}, \text{discussed below})\), the effect of drop triangulation becomes more significant but remains acceptable (see figure 4.4a, \(Ca = 0.9, 0.85\)). Near critical conditions, squeezing times are more sensitive to particle mesh resolution, as shown for \(Ca = 0.9\) in figure 4.4b. While we often made use of higher resolutions in the following results, generally \(\tilde{N}_\Delta \geq 11.5K\) is deemed acceptable. Excellent agreement between all tested convection schemes is observed at moderate-to-high viscosity ratios, for which all tested methods are stable (figure 4.3a). To confirm convergence at low viscosity ratio, where not all convection schemes can be tested, a high-resolution (\(\tilde{N}_\Delta = 20K, \tilde{N}_\Delta = 20K\)) run was completed using the upwind FV scheme at near-critical conditions (\(Ca = 0.9, \lambda = 0.1, \beta = 0.05\)). The drop squeezing time agrees to within <1.0\% with the ‘standard’ resolution (\(\tilde{N}_\Delta = 15.4K, \tilde{N}_\Delta = 11.5K\)) result. In addition, close agreement is found between the results by upwind FV and FBLS schemes (see §4.5.3); these are the only two stable schemes for squeezing simulations at small \(\lambda\).

The effect of initial droplet position, including vertical distance and horizontal offset from the constriction centre, on squeezing behavior was quantified. Doubling the initial vertical offset (from the default 6) to 12 had no measurable effect on squeezing times for the range of \(\beta\) used in this study, even at near-critical conditions (\(Ca = 0.9, \lambda = 4.0\)). This result is consistent with the fact that the maximum local change in surface tension is small (\(\approx 0.1\%\)) on the first time step, for the default initial position. When the drop is initially placed with a horizontal offset from the constriction center, there is a strong inclination for it to bypass the solid particles altogether. For example, using the default initial separation but shifting the drop halfway (or even quarterway) from directly above the constriction to directly above a spherical particle, results in the drop flowing around the three spheres. When offsetting the drop one eighth of this distance, the drop collides with the particle before moving into the constriction and quickly relaxing into its familiar shape. Due to this relatively fast drop relaxation, the minimum drop velocity, and surfactant
Figure 4.4: Convergence of results with respect to mesh resolution \((\lambda = 4.0, \beta = 0.05)\). (a) Solid lines \((\tilde{N}_\Delta = 20\text{K}, \hat{N}_\Delta = 8.6\text{K})\), and dashed lines \((\tilde{N}_\Delta = 11.5\text{K}, \hat{N}_\Delta = 8.6\text{K})\) show that the effect of droplet mesh resolution with the least-squares scheme is negligible except at near-critical conditions. (b) Convergence of drop velocity with respect to solid-particle triangulation at slightly supercritical \(Ca\).

distribution at this point, are negligibly affected, but squeezing times are increased due to slower droplet approach.

### 4.5.2 Capillary Number

The evolution of surfactant on the surface of a tight squeezing drop is shown in figure 4.5. The system represents behavior at low drop contamination \(\beta = 0.05\), moderately high viscosity ratio \(\lambda = 4.0\) and slightly supercritical capillary number \(Ca = 0.9\). The drop is subject to compressional flow as it approaches the constriction, and the initially uniformly-distributed surfactant is advected toward the drop’s equator. Surfactant predominately concentrates above the interstices of the solid particles, where densities reach approximately three times the equilibrium value. Marangoni stresses resist further accumulation in these regions and, at this moderate-to-high viscosity ratio, prevent the formation of steep concentration gradients until the drop has begun to enter the constriction. By \(t = 82\), the drop has nearly coated the solid obstacles. Due to the drop being driven by a uniform far-field flow, rather than settling under gravity,
The critical capillary number is decreased as compared to a clean drop. Near-critical contaminated drop squeezing can be summarized by the stages (I) development of a typical trapped state, (II) surfactant accumulation at the downwind pole and (III) eventual elongation of the drop tip. Internal circulation develops that allows for diverging surface flow. Near-zero surfactant concentrations develop quickly on both the upstream-facing (top) surface and in the dimple regions of the drop, falling below $\Gamma \sim 10^{-3}$ by $t \sim 95$ and decreasing to $\Gamma < 10^{-5}$ by $t = 272$. While Marangoni stresses tend to make the transition between depleted and concentrated regions more diffuse, they are unable to refill depleted areas until long after the drop has exited the constriction. A clean drop ($\beta = 0$) with otherwise equivalent parameters would be subcritical at $Ca = 0.9$, resulting in a trapped state. The mechanism by which the critical capillary number is decreased by drop contamination is summarized by snapshots I, II, and III in figure 4.5. At $t = 137$, the drop reaches a position and shape similar to that of a trapped clean drop. The surfactant that has collected above interparticle interstices is gradually swept downwind by the inner-constriction flow field. Surfactant accumulates at the downwind pole, locally decreasing surface tension and enhancing deformation and elongation of the drop tip. Once the leading edge of the drop
successfully passes through the constriction the remainder of the drop is able to follow. The drop exits the constriction with a highly nonuniform surface tension, with almost all surfactant located at the leading tip. While the trailing end is still near the constriction centre, such as at \( t = 553 \), the droplet develops into a shape similar to a pendant drop. During this stage, surfactant concentrations at the leading tip increase to eight times the original concentration, as seen in figure 4.6d. Far downstream, the drop returns to spherical with uniform surfactant concentration.

As with clean drops, capillary number has a strong effect on contaminated drop squeezing. The temporal dynamics in a wide range of capillary numbers are provided in figure 4.6, using high resolutions (\( \tilde{N}_\Delta = 20K, \tilde{N}_\Delta = 20K \)) for the near-critical \( Ca = 0.9 \). As seen in figure 4.6a, the critical capillary number \( (Ca_{crit}) \), below which trapping occurs, is observed to lie between \( Ca = 0.7 \) and \( Ca = 0.9 \). This value is consistent with a power-law regression of supercritical \( Ca \) against squeezing time \( (T_s) \) (a technique similar to that of Ratcliffe et al. (2010) for gravity-induced squeezing), which predicts a \( Ca_{crit} \approx 0.8 \) (figure 4.6b). In the present study, a squeezing drop is defined to have a velocity \( U \) less than 1.0% of the far-field velocity \( |u_\infty| \). A similar analysis of previous work (Zinchenko & Davis, 2006) indicates that \( Ca_{crit} \approx 1.0 \) for clean drops, corresponding to an \(~20\%\) decrease in \( Ca_{crit} \) at low degrees of contamination (\( \beta = 0.05 \)) and moderately high viscosity ratios (\( \lambda = 4.0 \)). The minimum gap between drop and solid particles is a relatively weak function of capillary number and is similar to that for clean drops. Notably, for a contaminated drop, cusps in gap vs. time are more pronounced at various stages of the squeezing process (cf. figure 4.6c with figure 17 of Zinchenko & Davis (2006)).

The global minimum value of surface tension (\( \sigma_{min} \)) for a contaminated drop during the squeezing process is shown in figure 4.7a. Discontinuities in the derivative of \( \sigma_{min}(t) \) correspond to changes in the locale of maximum surfactant concentration, which occurs e.g. between \( t = 82 \) and \( t = 272 \) (figure 4.5). Decreasing capillary number tends to decrease the variation of \( \sigma_{min} \), which for \( Ca = 0.9 \) remains between 5% and 10% less than \( \sigma_{eq} \) for the majority of drop tight-squeezing. The distribution of surface tension at local extrema of \( \sigma_{min}(t) \) during the squeezing process is shown in 4.7b. Notably, a linear equation of state appears sufficient to retain positive surface tension, despite the development of high surfactant concentrations. In conjunction with modifying local surface tension, the presence of surfactant is expected
Figure 4.6: Effect of capillary number on contaminated drop squeezing ($\lambda = 4.0$, $\beta = 0.05$). Resolution for $Ca = 1.5, 1.3$ ($\hat{N}_\Delta^{lo}: N_\Delta = 20K$, $\hat{N}_\Delta = 8.6K$). Resolution for $Ca = 1.1, 0.9$ ($\hat{N}_\Delta^{hi}$): $N_\Delta = 20K$, $\hat{N}_\Delta = 20K$.

(a) Drop dynamics under a range of sub-, super-, and near-critical capillary numbers. Dashed tie line is used to define squeezing times. (b) Power-law fitting of supercritical squeezing times ($\bullet$, numerical results) in order to extrapolate the critical value, $Ca = 0.80$. (c) Gap between drop and solid obstacles tends to decrease with capillary number. Dashed lines show effect of solid-particle resolution. (d) Evolution of surfactant concentrations for super- and subcritical $Ca$. Cusps in global maximum surfactant concentration indicate when $\Gamma_{max}$ shifts to a different locale on the drop surface.
Figure 4.7: Evolution of surface tension during contaminated drop squeezing through three-sphere constriction ($\lambda = 4.0, \beta = 0.05, \tilde{N}_\Delta = 15.4K, \hat{N}_\Delta = 11.5K$). (a) Global minimum value of surface tension. Labeled points on $Ca = 0.9$ curve shown in second panel. (b) Distribution of surface tension at various local extrema of $\sigma_{min}(t)$ at $Ca = 0.9$. Solid particles not shown.

to affect surface mobility. A global metric for interface mobility can be defined as the surface average ($\overline{S}$) of $|u_s|$, where $u_s$ is the magnitude of the tangential fluid velocity $u_s$. As seen in figure 4.8, a trapped clean drop reaches a steady-state surface mobility ($|u_s|\overline{S}$) that is much higher than $U$, due to internal circulation. Despite maintaining a higher $U$ during squeezing, a contaminated drop has lower surface mobility, as compared to a clean drop, due to Marangoni stresses resisting surface flow. However, the low degree of contamination ($\beta = 0.05$) is unable to completely immobilize the surface, driven by the far-field flow.

Several contaminated trapped states are compared to that of a moderately subcritical clean drop ($Ca = 0.9$) in figure 4.9 for $\lambda = 4.0$. To obtain a similar trapped-drop shape at low surfactant loading, $Ca$ must be decreased to 0.7. A clean drop has a $Ca_{crit} \approx 1.0$, and the contaminated system has a $Ca_{crit} \approx 0.8$, so in both cases that characteristic shape is obtained when $Ca$ is $\sim 0.1$ less than $Ca_{crit}$. For a near-critical contaminated drop such as for $Ca = 0.8$, a significant portion of the drop, including the majority of highly-concentrated surfactant, may extend past the centre of the constriction and remain in a stable trapped state (figure 4.9). A contaminated trapped drop, according to mass balance, should become immobilized at steady state in regions with nonuniform surfactant concentrations. The effect of low
Figure 4.8: Effect of low surfactant contamination on drop interface mobility \((Ca = 0.9, \lambda = 4.0, \tilde{N}_\Delta = 20K, \tilde{N}_\Delta = 11.5K)\), quantified as the surface average of \(|u_s|\), where \(u_s\) is the magnitude of tangential velocity. The interface mobility of flow-driven tight-squeezing drops remains relatively high due to internal circulation. Surfactant decreases interface mobility due to the presence of resistive Marangoni stresses.

Contamination on steady-state interfacial velocities is shown in figure 4.10. Due to the use of higher-order singularity subtraction in the boundary-integral algorithm, drop velocity can stably decrease by more than four orders of magnitude, at which point a drop is assumed to be in a trapped state. The effect of contamination on surface velocity becomes transparent when viewed with a logarithmic scale: regions containing surfactant show a marked decrease in velocity, including the development of a ‘stagnant cap’ on the downwind pole. Additionally, surfactant modifies the overall flow field. Rather than divergent interfacial velocity at the approximate centre of the dimple as is characteristic of clean drops, the entirety of the dimple region develops a flow opposed to the far-field direction, and elongated vortices develop along its edges (figure 4.10). The effect of this modified surface velocity field on the minimum drop-solid separation is weak, with the gap between ~0.011–0.012 in both cases, at steady state. However, in the contaminated system, the thickness of the lubrication layer is more uniform, as discussed in §4.5.4.
Figure 4.9: Effect of low surfactant contamination on the shape of steady-state trapped drops ($\lambda = 4.0$, $\tilde{N}_\Delta=20K$, $\tilde{N}_\Delta = 11.5K$) at various capillary numbers. A moderately subcritical clean drop ($\beta = 0.0, \Gamma_{eq} = 0.0$), for reference, is shaded to reveal 3D structure. A significantly lower $Ca$ is required for a similar contaminated-drop trapped shape. Dashed line indicates constriction centre. Drop is rotated to show dimpled face; solid particles not shown.

Figure 4.10: Surfactant contamination tends to decrease the interfacial velocity magnitude ($u_s$) of steady-state trapped drops ($\lambda = 4.0$, $\tilde{N}_\Delta=20K$, $\tilde{N}_\Delta = 11.5K$). Velocities are binned using colors according to a logarithmic scale. Large arrows indicate the general shape of the velocity field, which is affected by contamination. Drop is rotated to show dimpled face; solid particles not shown.
4.5.3 Viscosity Ratio

Low viscosity ratios, $\lambda \sim 0.1$ or less, pose a significant hurdle for numerical treatment of convection-dominated surfactant transport in complex flow fields. Single drops in simple shear flow have been reported to demonstrate unphysical negative surface tension within relevant parameter ranges, regardless of the governing equation of state (Bazhlekov et al., 2006). A similar issue is encountered for tight squeezing when using prior LS or FV convection schemes, regardless of whether implicit, explicit or semi-implicit time integration is used to advance surfactant concentrations. Visualizing the simulation at every time step leading up to the crash reveals that it is typically a single node near high concentration gradients that is rationed an erroneously high level of surfactant. Advection of non-diffusive scalar fields, e.g. within flows that may include sharp density gradients or shock waves, is common in inviscid fluid flow modeling. It is standard to convect such fields with an upwind scheme, an integration technique that is biased toward velocities upstream of the control volume and exhibits increased numerical stability. The only convection methods tested in this study that were stable for tight squeezing of low-viscosity-ratio drops are the first-order upwind FV and FBLS schemes for unstructured meshes. For all runs that showed no signs of unphysical behavior, regardless of the convection method used, the minimum value of surface tension ($\sigma_{\text{min}}$) remained above $\sigma_{\text{min}} \gtrsim 0.5$. Therefore, Marangoni stresses appear sufficient to prevent the development of unphysical negative surface tension in these systems even when coupled to a linear equation of state.

As shown in figure 4.11a, the dependence of contaminated drop squeezing dynamics on viscosity ratio follows a trend similar to that of clean drops at supercritical capillary numbers (Zinchenko & Davis, 2006). However, the evolution of surfactant becomes steadily more complex, as seen in figure 4.11b, due to its ability to more quickly respond to the transient stress field at the interface. Recall that discontinuities in the derivative of $\sigma_{\text{min}}$ generally correspond to a change in the locale of maximum surfactant concentration. For example, additional cusps in $\sigma_{\text{min}}$ vs. time appear for lower $\lambda$, approximately when the drop is halfway through the constriction (see figure 4.11b: $\lambda = 0.1$, $t \approx 250$). Visualizing the evolution of surfactant at this time reveals that the high surfactant concentration at the leading tip is briefly transported away, back toward and through the centre of the constriction, presumably driven by
Marangoni stresses (figure 4.12). This effect ultimately results in the drop exiting the constriction with a bimodal distribution of surfactant, having high concentrations at both the leading and trailing poles of the drop, in contrast to just the downwind pole as observed with higher viscosity ratios (figure 4.5).

Transient surfactant distributions for $\lambda = 0.1$ and $\lambda = 4.0$ are shown in figure 4.13, at the time of global drop velocity minimum ($U_{\text{min}}$) of their respective squeezing trajectories. Surfactant-concentration extrema tend to be amplified by lower viscosity ratios, at analogous stages in the squeezing process. At $U_{\text{min}}$, the inner constriction flow field has swept significant amounts of surfactant to the downstream pole, reaching $\Gamma_{\text{max}} = 2.9$ for $\lambda = 0.1$ and $\Gamma_{\text{max}} = 2.6$ for $\lambda = 4.0$. Sharper surfactant gradients are observed for $\lambda = 0.1$, particularly at the ‘triple point’ upstream from particle interstices. This point is typically where numerical difficulties arise with convection methods other than the flow-biased schemes. Also, Marangoni stresses become strong enough to partially refill depleted dimple regions, which begin with relatively uniform near-zero concentrations at the onset of squeezing, to a greater extent at low viscosity ratios.
CHAPTER 4. SINGLE DROP SQUEEZING WITH INSOLUBLE SURFACTANT

4.5.4 Degree of contamination

The degree of surfactant contamination, quantified by the elasticity parameter ($\beta$), is most influential on squeezing dynamics at near-critical capillary numbers or low viscosity ratios. For example, no appreciable difference in squeezing times is observed between $\beta = 0.05$ and $\beta = 0.2$ at high capillary number and viscosity ratios ($Ca = 1.3$, $\lambda = 4.0$). However, at $Ca = 0.85$, increasing from low ($\beta = 0.05$) to medium ($\beta = 0.1$) degrees of contamination considerably decreases squeezing times (figure 4.14a). For $\beta \leq 0.1$, $T_s$ obeys the power-law relation provided in figure 4.14b. Extrapolating to a trapped state ($T_s \to \infty$) would imply that $\beta_{crit} = 0.03$ for this system. For $\beta$ above a maximum value, further increases in degree of contamination have a negligible effect on squeezing times (figure 4.14b). This effect could be of interest, e.g., to the field of enhanced oil recovery, for which diminishing returns are observed when surfactant levels are raised above a certain value.

The same trend is observed for low viscosity ratios ($\lambda = 0.1$). As seen in figure 4.15(a, b), squeezing times remain almost constant for $\beta \gg 0.1$. To isolate the mechanism for this behavior, we searched for other system parameters that follow a similar trend with respect to $\beta$. The minimum gap between drop and particle during early drop squeezing is shown in figure 4.15c. During initial droplet approach, there is
Figure 4.13: Effect of viscosity ratio on surfactant distribution ($Ca = 0.9, \beta = 0.05$) at analogous points in the squeezing process ($U_{\text{min}}$). One of the three solid spheres comprising the constriction is shown for reference, rendered in translucent gray. (a) Low viscosity ratio results in higher maximum concentrations ($\sigma_{\text{min}} = 0.90, \Gamma_{\text{max}} = 2.9$) and steeper gradients. (b) Analogous snapshot of surfactant distribution for high viscosity ratio and moderately supercritical $Ca$ ($\sigma_{\text{min}} = 0.92, \Gamma_{\text{max}} = 2.6$).

Figure 4.14: Effect of elasticity parameter (degree of contamination) on squeezing dynamics ($Ca = 0.85, \lambda = 4.0, \tilde{N}_\Delta = 20K, \tilde{N}_\Delta = 8.6K$). (a) Degree of contamination has an appreciable effect on squeezing times at near-critical conditions. (b) Elasticity parameter vs. squeezing times exhibits a power-law fit below a maximum value (solid circles), above which increasing $\beta$ has negligible effect on $T_s$. Outlying (unfitted) data points denoted by X marks.
a clear trend of smaller separation with decreasing contamination, which can be attributed to surfactant’s
effect on the lubrication layer, as discussed below. However, because this initial gap disparity quickly
converges, it is not expected to influence overall squeezing times. As observed for capillary number, there is
a very weak dependence of gap on degree of contamination for the majority of the squeezing process, being
essentially independent after \( t \geq 100 \). A metric for the evolution of the surfactant concentration is shown in
figure 4.15d. To directly compare surfactant concentration vs. degree of contamination, concentration is
scaled by \( \beta \) and shifted according to its initial value. The metric \( \Delta(\beta \Gamma_{\text{max}}) = \beta \Gamma_{\text{max}} - (\beta \Gamma_{\text{max}})_{eq} \)
represents the relative increase in surfactant concentration. This metric appears to be converging at local
extrema, for example at \( t \approx 20 \), with respect to increasing \( \beta \). Recall that the first local minimum of \( \Gamma_{\text{max}} \)
(\( t \approx 65 \)) represents the shift in location of \( \Gamma_{\text{max}} \) from the drop equator to the leading tip of the drop (see
the inset of figure 4.15d). A clear trend is the gradual decrease in the right derivative of \( \Gamma_{\text{max}} \) at the cusp,
indicating that at low viscosity ratios and high degrees of contamination, Marangoni stresses almost
immediately begin to draw surfactant away from the leading tip as it begins to pass through the
constriction.

Average surface mobility continues to decrease with increasing contamination, for the majority of
the squeezing process, as shown in figure 4.16a. This trend also indicates the continued increase in the
strength of Marangoni stresses with respect to hydrodynamic stresses. The distribution of surfactant and
surface flow field are also significantly affected by increasing contamination. Surface velocities for various \( \beta \)
values are shown in figure 4.16b, at respective global minimums of drop velocity. The distribution of
surface velocities also indicates key regions of surfactant distribution; e.g., the surface extensional flow
indicated by arrows corresponds to the sharp surfactant gradient universally observed on the top surface.
With increasing contamination, this sharp gradient nears the top pole of the drop, to the point of almost
vanishing for \( \beta = 0.15 \). The disappearance of this near-zero concentration region, along with a similar
filling of surfactant into near-contact regions, results in almost the entire drop surface hosting a significant
amount of surfactant. The presence of surfactant generally results in dramatically decreased tangential
velocity, as is visually apparent by the receding region of \( u_s > 10^{-2} \) on the top surface.

To examine the effect of degree of contamination on droplet trapping, a systematic study of critical
Figure 4.15: Effect of elasticity parameter on squeezing dynamics at low viscosity ratio ($Ca = 0.9, \lambda = 0.1, \tilde{N}_\Delta = 15.4K, \tilde{N}_\Delta = 11.5K$). (a) Drop dynamics for a range of degree of contamination. (b) Power-law fitting of squeezing times. Outlying (unfitted) data points denoted by X marks. (c) Drop-particle gap is sensitive to contamination for $t < 100$. (d) Evolution of surfactant concentration with respect to contamination. For direct comparison, $\Gamma_{max}$ is scaled by $\beta$ and shifted by $(\beta \Gamma_{max})_{eq}$ for super- and subcritical $Ca$. Inset: shift of $\Gamma_{max}$ to the leading tip of the drop.
Figure 4.16: Effect of degree of contamination on interface mobility ($Ca = 0.9$, $\lambda = 0.1$, $\tilde{N}_\Delta = 15.4K$, $\tilde{N}_\Delta = 11.5K$). (a) Surface mobility steadily decreases with increasing contamination. (b) Distribution of tangential velocity, binned on a logarithmic scale, for various $\beta$ at respective global minimums of squeezing velocity. The location of surface extensional flow, indicative of a sharp surfactant-concentration gradient, highlighted with arrows. Drop is rotated to show dimpled face; solid particles not shown.
capillary number was completed at unit viscosity ratio, shown in figure 4.17. As was noted for $\lambda = 4$, a
dramatic reduction of $Ca_{\text{crit}}$ is observed between clean drops ($\beta = 0$) and $\beta = 0.05$, decreasing by 25% in
this case ($\lambda = 1$). The intervening data reveal that the dependence is nearly linear within this range of $\beta$
values. Above $\beta \approx 0.1$, $Ca_{\text{crit}}$ remains almost constant, indicating a minimum degree of contamination in
order to maximize droplet pass-through, e.g. when capillary number is uncertain. Similar to the the effect
of $\beta$ on squeezing times at fixed $Ca$, the lack of dependence of $Ca_{\text{crit}}$ on degree on contamination above a
certain $\beta$ value is attributed to tangential immobilization of the interface.

Finally, we consider the effect of contamination on the lubrication layer. As mentioned above,
increasing $\beta$ has negligible effect on the minimum drop-particle separation for $t > 100$, but tends to result
in a larger gap during early stages of drop squeezing. An interesting aspect of the gap evolution is the
appearance of two cusps in gap vs. time, especially at low viscosity ratio and low contamination (figure
4.15c). For $\beta = 0.05$, these singularities occur at $t \approx 80$ and $t \approx 103$, with the drop-particle gap converging
with other $\beta$ values at the second point. To view the lubrication layer during these times, we consider a
Figure 4.18: Cutaway of droplet squeezing through three-sphere constriction, showing lubrication layer ($Ca = 0.9$, $\lambda = 0.1$, $\tilde{N}_\Delta = 15.4K$, $\tilde{N}_\Delta = 11.5K$). Planar cross-section passes through the centre of the constriction and one particle. (a) Contaminated drop squeezing ($\beta = 0.05$). Arrows indicate the general direction of interfacial movement. The expanding drop tip is observed to most closely approach the surface of the particle. (b) Snapshot of clean drop planar cross-section at the same capillary number and viscosity ratio ($\tilde{N}_\Delta = 20K$, $\tilde{N}_\Delta = 20K$).

planar cross-section of the system, passing through the constriction and particle centres, as shown in figure 4.18a. Interestingly, especially for $t \leq 80$, the lubrication layer is quite uniform; in contrast, for clean drops a more pronounced dimple is observed, even after accounting for the curvature of the spherical surface (see figure 4.18b). The transition between $t = 103$ and $t = 120$ reveals that it is the leading tip of the drop that most closely approaches the solid particle, notably breaking the uniformity of the lubrication layer. The expansion of the drop tip toward the particle surface is responsible for the monotonic decrease of drop-solid separation, and this gap is independent of degree of contamination.

4.6 Remarks on incorporating surfactant into multiphase BIM simulations

The behavior of tight-squeezing drops contaminated with insoluble surfactant was investigated using high-resolution, 3D boundary-integral simulations. The drops are freely-suspended in a uniform far-field flow, and the constriction is composed of three solid particles fixed in space. Drops are initially spherical with a uniform surfactant distribution, and a linear equation of state relates surfactant concentration to
surface tension. Stable modeling of near-critical capillary numbers and trapped states is enabled by the
desingularization techniques developed by Zinchenko & Davis (2006, 2017a). The boundary-integral
formulation precisely resolves the fluid-fluid interface, allowing for the straightforward implementation of
several distinct convection schemes for surfactant transport. Upwind-biased schemes were found to be the
most stable and were required to model tight squeezing for certain parameter ranges of interest, such as
low viscosity ratios ($\lambda \lesssim 0.25$). Drop squeezing is characterized with respect to capillary number, viscosity
ratio and degree of contamination, $\beta$.

The evolution of surfactant on the drop surface is visually similar for all parameter ranges of
interest. A characteristic aspect of contaminated tight squeezing is the development of sharp
surfactant-concentration gradients. These gradients develop quickly at the onset of squeezing due to the
competition between advection of the interface and resistive Marangoni stresses. Due to the compressional
flow upstream from a constriction, surfactant concentrates around the drop equator, in particular at
regions above solid-particle interstices. During the development of a typical trapped-drop shape, the top
surface and near-contact regions are host to almost zero surfactant, especially at low degrees of
contamination. Surfactant is gradually swept to the leading tip of the drop, decreasing local surface tension
and allowing passage through the constriction, and the remainder of the drop quickly follows. Although the
evolution of drop shapes resembles that of tight-squeezing clean drops, contamination and the resulting
variable local surface tension significantly affects squeezing dynamics.

The addition of small amounts of surfactant decreases the critical capillary number and modifies the
interfacial velocity field. A small degree of contamination, $\beta = 0.05$, is found to decrease the critical
capillary number for squeezing $Ca_{crit}$ from $\sim 1$ to $\sim 0.8$ for $\lambda = 4.0$. The mechanism of near-critical
contaminated drop squeezing can be summarized by three stages: development of a typical trapped state,
surfactant accumulation at the downwind pole, and subsequent elongation of the drop tip. The interfacial
flow field is also significantly modified by the presence of surfactant. The tangential surface velocity is
decreased in regions of nonzero surfactant, particularly at the leading tip. For a clean drop, a divergent
surface velocity is observed at the approximate centre of the drop dimple. For contaminated drops, the
entirety of the near-contact region has an interfacial velocity in a direction opposing that of the far-field
flow. For a trapped drop at $\lambda = 4.0$, resistance from Marangoni stresses governed by a linear equation of state are sufficient to keep local surfactant concentrations within $\sim 3$ times the equilibrium value.

The influence of surfactant is most prominent at low viscosity ratios. Extremely sharp surfactant gradients develop even within the compressional flow upstream from the constriction. The surfactant distribution more quickly responds to the transient stress field, enhancing the ability of Marangoni stresses to partially refill surfactant-depleted near-contact regions. During the later stages of squeezing, this increased responsiveness allows surfactant accumulated at the leading tip to be ‘pulled’ back through the constriction, resulting in a bimodal distribution at exit. Although the evolution of surfactant becomes more complex at low viscosity ratios, squeezing times as a function of viscosity ratio follow a similar trend as that of clean drops. Even at the low viscosity ratio $\lambda = 0.1$ and moderately supercritical conditions ($Ca = 0.9, \beta = 0.05$), Marangoni stresses governed by a linear equation of state are sufficient to retain positive values of surface tension. During the early and middle stages of tight squeezing, which is most representative of squeezing through large-scale granular media, $\sigma$ remains within 20% of $\sigma_{eq}$.

Critical capillary number and drop squeezing time decrease with increasing degree of contamination, up to a certain saturation $\beta$-value above which increasing $\beta$ has negligible effect. For unit viscosity ratio, the maximum drop in $Ca_{crit}$ due to contamination is as much as 27%. In all cases, this saturation occurs at $\beta \approx 0.1$. The phenomenon of diminishing returns with respect to increasing surfactant may be of interest e.g. to the field of enhanced oil recovery. The trend is characterized by the increasing strength of Marangoni stresses, which effectively limit the maximum surfactant concentration. In addition, for highly-contaminated surfaces, the surface area of near-zero surfactant regions decreases considerably, resulting in the disappearance of sharp concentration gradients and the steady decrease of average surface mobility. It is concluded that surfactants have a significant impact on the hydrodynamics of fluid-fluid interfaces under tight-squeezing conditions, generally increasing the ease with which drops can pass through tight constrictions.

On the methodological side, an essential finding of the present work is in understanding the origin of negative surface tensions sometimes observed in prior simulations for concentrated contaminated emulsions in the limit of non-diffusive surfactant (Zinchenko & Davis, 2017a). This artifact happens to arise from
numerical instability of prior surfactant transport schemes and is not a physical deficiency of the linear
equation of state for surfactant. The upwind finite-volume (FV) and substantially new flow-biased
least-squares (FBLS) schemes implemented herein resolve this issue, at least for drop squeezing simulations.
As a general tool for surfactant transport on a deformable surface, our upwind FV implementation is
probably most stable, although it comes with resolution-dependent numerical diffusion (somewhat larger
than for FBLS). Close agreement between the results by these two, very different schemes demonstrates
that the limit of non-diffusive surfactant is nevertheless achieved in the present simulations.
Chapter 5

Flow of emulsions with insoluble surfactant through porous media

By law of periodical repetition, everything which has happened once must happen again and again – and not capriciously, but at regular periods, and each thing in its own period, not another’s and each obeying its own law.

-Mark Twain

Synopsis

A pressure-driven, periodic emulsion flowing at small Reynolds number through a cubic array of spheres is modeled using a three-dimensional boundary-integral algorithm, by considering one droplet in a repeating unit cell. The solid phase is fixed in space and fills 50% of the periodic cell by volume, creating pores connected by interparticle constrictions (pore throats). The emulsion is initially uniformly-coated with surfactant, which is subsequently advected using a robust algorithm for insoluble surfactant transport. Drop surface tension is related to the surfactant concentration by a linear equation of state. Two emulsions concentrations are considered, 36% and 50% of the void volume, and in both cases the non-deformed droplet size is on the scale of the particle size and considerably larger than the pore throat. The
permeability of each phase is studied versus degree of contamination and capillary number. The emulsion quickly reaches a regular period of motion, for which the average drop-phase velocity is higher than that of the continuous phase, resulting in surfactant being swept to the trailing half the droplet. Away from critical conditions, emulsions with a low degree of contamination have a longer period of motion as compared to a clean emulsion, and this period increases incrementally with further increases in degree of contamination. In contrast to clean drops, a notable shift in contaminated-droplet squeezing trends is expected to occur near critical squeezing conditions, due to the redistribution of surfactant when the drop-phase velocity falls below the continuous-phase velocity.

5.1 Confined and contaminated emulsions: prior knowledge

While our understanding of surfactants’ effect on single-drop dynamics has recently been improving, the general rheology of confined and contaminated emulsions remains less characterized. In particular, complex multiscale behavior results when the drop size is larger than granular interstices. In such cases, the emulsion cannot be treated as a single phase and a droplet-resolved model is required. Such insight can be achieved either via experiment through advanced imaging techniques or by numerical simulations, and stands to benefit the fields of enhanced oil recovery (EOR), biomicrofluidics applications, and pharmaceutical and food manufacturing processes. From a numerical standpoint, several exacting and coupled physical phenomena need to be resolved with high fidelity. Droplets in tight-squeezing situations tend to approach solid interfaces very closely, requiring lubrication forces to explicitly be included. Similarly, liquid-liquid interfaces are also in close proximity within high-density emulsions. The presence of surfactant on each droplet interface adds additional dynamics, including variable surface tension and Marangoni stresses, which affect both fluid-fluid and fluid-solid lubrication properties. We present a boundary-integral formulation to capture the essential physics of this confined and contaminated system, to obtain a deeper fundamental understanding of how surfactant influences individual droplets’ interaction with neighboring drops and the confining porous media, as well as the overall rheology of these systems.

Surfactant-laden flows and emulsions are commonly discussed in the context of subsurface transport,
where they can be formed \textit{ex situ} by high-shear mixing, high-pressure homogenization, etc., or \textit{in situ} whether intentionally or not. Purposeful addition of surfactants by chemical injection is used as an EOR technique and for soil decontamination, while biosurfactants are produced naturally by microorganisms (Ouyang \textit{et al.}, 1995). Thomas & Farouq Ali (1989) established that the drop-to-pore size ratio and injection pressure are key factors of emulsion mobility in porous media. The increase in apparent viscosity of subsurface flows caused by emulsification can be considered a positive or negative effect, depending on the application. During surfactant-enhanced soil flushing to remove contaminants, the formation of macroemulsions and the resulting decrease in soil permeability are considered an adverse effect (Crawford \textit{et al.}, 1997). For oil recovery, increasing the resistivity of highly-permeable parts of a reservoir can be beneficial, by forcing liquid into low-permeability regions and improving the sweep efficiency (Lu \textit{et al.}, 2018; Zhou \textit{et al.}, 2018a). Attention has increasingly been given to pore-scale events, e.g., identification of the critical capillary number below which droplets are able to effectively block pores, a value that depends on the drop-to-pore radius ratio (Moradi \textit{et al.}, 2014). Fundamental understanding of the physics of contaminated emulsions becomes increasingly important for advanced techniques, such as selective mobility control of emulsion flows (Guillen \textit{et al.}, 2012b) and spontaneous emulsification (Li \textit{et al.}, 2020).

Experimental models for investigating confined multiphase flow range from simple channels to pore-scale-resolved samples of tortuous sandstone, with the former having more direct application in microfluidics. Huerre \textit{et al.} (2015) noted that the lubrication behavior between a droplet and its confining wall is sensitive to capillary number, and used a high concentration of insoluble surfactant to track interfacial velocities. In the case of a train of droplets interacting with hydrodynamic traps, Bithi & Vanapalli (2010) demonstrated the importance of tuning the drop-phase fluid and surfactant properties to obtain the desired droplet trapping behavior. For example, they concluded that lowering the drop-phase viscosity allows for more uniform trapping at larger flow rates, in their system. Bremond \textit{et al.} (2008) discovered an interesting effect related to surfactant-stabilized droplet pairs in a microfluidic channel, namely that it is the separation of drops that can cause their coalescence, as opposed to their approach. More comprehensive reviews on the role of surfactants in channel flows are provided by Baret (2012) and Guido & Preziosi (2010).
Experimental setups that more closely mimic porous media include emulsion flow through glass spheres, sand or other granular media, and highly-convoluted networks with a distribution of pore-sizes. Several pore-scale events can result in droplet trapping in a bed of glass beads, with clogging either caused by a single droplet having a non-deformed radius on the order of the pore-throat size, or by many droplets significantly smaller than the pore, which can jam to form mechanically-stable arches across the pore-site (Guillen et al., 2012a; Lu et al., 2018). Non-Newtonian behavior of multiphase flow was confirmed for an oil-in-water emulsion flowing under pressure through sand packs, and specifically observed to follow power-law fluid dynamics (Mandal & Bera, 2015). Oughanem et al. (2015) used micro-computed tomography to determine oil ganglia size distributions and resolve individual droplet-pore interactions (e.g., see figure 8 therein), for a variety of types of sandstone. They determined the relative permeability of the carrier fluid with respect to capillary and Bond numbers, and established scaling relationships between fluid properties and permeability in certain regimes. Mirchi et al. (2019) completed similarly-resolved experiments to probe the effect of surfactant types on the recovery of nonwetting trapped phases from porous media, concluding that nonionic (as opposed to anionic) surfactants are more effective in breaking up trapped oil clusters into smaller droplets. Finally, recent work by Wang et al. (2020) suggests there is an optimal surfactant content for emulsion-oriented oil recovery, with respect to the viscosity reduction of heavy oil that enhances oil recovery. More extensive reviews have been offered by Zhang et al. (2018) and Perazzo et al. (2018).

Computer modeling of emulsions range across a similar range of scales and milieus. Very large-scale descriptions make use of a two-phase extension of Darcy’s law (Kalaydjian, 1990) or network modeling (Romero et al., 2011). Herein we limit our discussion to droplet-resolved simulations. Borhan & Mao (1992) used the boundary-integral to simulate 2D droplets flowing through a circular channel, concluding that small amounts of surfactants retard the motion of drops at large Péclet number, due to immobilization of the interface. Janssen & Anderson (2008b) came to a similar conclusion for (3D) surfactant-laden drops between parallel plates. Hanna & Vlahovska (2010) elucidated the ability of non-uniform surfactant distributions to affect droplet migration. Zinchenko & Davis (2013) completed a large-scale study of clean emulsions (up to 100 drops) flowing through a packed bed of spheres (up to 36 particles), and accounted...
for drop breakup, which occurred frequently at sufficiently high capillary numbers. It was found that steady average values for the drop-phase and emulsion-phase velocities were reached quickly after the start of the droplet-breakup cascade. An overview of modern 3D boundary-integral methods for emulsion flows interacting with solid phases is provided by Zinchenko & Davis (2017b).

Other popular numerical techniques used to tackle complex multiphase problems include the volume-of-fluid, smoothed-particle hydrodynamics, and lattice-Boltzmann methods. Cleret de Langavant et al. (2017) used the volume-of-fluid and level-set methods to model the effect of soluble surfactant on droplet interfaces in a variety of circumstances, including drop breakup under shear flow and the interaction of free surfaces with solid substrates. The effect of surfactant on multiple drops in 3D circular channels was investigated by Hasan & Farhat (2018), revealing a depleted surfactant concentration in the frontal zone of the drop interface, especially for the leading member of a droplet train. Luo et al. (2018) considered an insoluble-surfactant-laden drop in a square channel, using a front-tracking finite-difference method, demonstrating that different channel shapes can result in notably different (quantitative) surfactant distributions and droplet behaviors. Liu et al. (2018) introduced a hybrid lattice-Boltzmann and finite-difference method for the interaction between confined droplets, indicating that the critical capillary number for drop breakup follows different trends for drops contaminated with insoluble surfactant than for clean drops. Zhou et al. (2018b) provided a direct comparison between experiments and simulations for single-pore behavior, and found that the size of droplets formed within porous media are mostly on the order of the pore-throat diameter. Alpak et al. (2019) simulated large-scale two-phase flows through digital scans of real limestone and sandstone samples, using a phase-field lattice-Boltzmann method. Studies that incorporate the effect of surfactant into large-scale, droplet-resolved simulations of emulsions in porous media seem to be missing from the literature.

In the present work, we combine several recent efforts, one of which introduced a boundary-integral formulation for deformable drops either passing between or becoming trapped between solid spheres, and the second of which established a robust formulation for surfactant transport on the surface of tight-squeezing drops. Zinchenko & Davis (2008a) demonstrated the feasibility of multidrop-multiparticle simulations using the boundary-integral method, after employing a certain representation for solid-particle
contributions (the Hebeker density) and a suite of desingularization tools, including high-order singularity subtraction. The methodology was applied to characterize the dynamic behaviour of a periodic emulsion squeezing through a simple cubic lattice composed of spheres (Zinchenko & Davis, 2008b). Gissinger et al. (2019a) showed that surfactant can decrease the critical capillary number for drop squeezing, in the case of single droplets embedded in a far-field flow, at least up to a point above which adding more surfactant does not affect squeezing dynamics. Herein we answer the question: how does surfactant affect the squeezing of a periodic emulsion in a simple cubic lattice? The problem formulation, relevant system parameters and initial configurations for moderate- and high-density emulsions are provided in §5.2. Details of the boundary-integral formulation for a contaminated, high-density emulsion flowing through an array of spheres are given in §5.3. The results of numerical simulations are discussed in §5.4, and concluding remarks are provided in §5.5.

5.2 Problem formulation: specifications for the emulsion and solid phase

Consider a single droplet $\tilde{S}$ surrounded by a carrier fluid and within a cubic box, periodic in all three dimensions, where Newtonian Stokes flow is assumed inside and outside the drop. An additional solid phase (fixed in space) is comprised of a single sphere $\hat{S}$, which due to the periodicity, forms a simple cubic array of pores connected by interparticle interstices, or pore throats (see figure 5.1). The droplet is initialized at the center of this pore, either as a sphere if the pore space permits, or ‘swelled’ and deformed to reach a particular ratio of emulsion concentration, as shown in figure 5.1b. The ‘swelling algorithm’ used to create the high-density emulsions is a simple, artificial method to prepare initial configurations, as detailed in Zinchenko & Davis (2008a). The mesh resolutions $\tilde{N}_{\Delta}$ and $\hat{N}_{\Delta}$ refer to the number of triangles in each solid-particle and drop mesh, respectively. The drop mesh resolution is fixed at $\tilde{N}_{\Delta} = 11520$, and the particle resolution is fixed at $\hat{N}_{\Delta} = 20480$, resolutions found to provide accurate results for contaminated drop tight-squeezing by (Gissinger et al., 2019a) (further convergence testing is underway).

In both cases, the surface of the droplet is initially covered in a uniform concentration of surfactant,
and local surface tension in relation to surfactant concentration using a linear equation of state, as described below. The emulsion flow is caused by a constant average pressure gradient \((\nabla p)\), assumed to be along the negative \(z\) axis. The characteristic length \(L\) is defined as the side length of the cubic periodic cell (see figure 5.1). The radii of the solid particle and non-deformed droplet are \(\hat{a}\) and \(\tilde{a}\), respectively, nondimensionalized by \(L\). The volume fraction of the solid phase with respect to the entire cell is 0.5 for all systems herein, resulting in a solid particle radius \(\hat{a} \approx 0.49\). The emulsion concentration is defined by the concentration by volume of the drop phase, with respect to the available space between solids. Two emulsions concentrations are considered in this work, 36% and 50%, resulting in non-deformed droplet radii \(\tilde{a} = 0.35\) and \(\tilde{a} = 0.39\), respectively (following Zinchenko & Davis (2008b)). The drop-to-medium viscosity ratio is \(\lambda = \mu_d/\mu_e\), where \(\mu_d\) and \(\mu_e\) are the drop-phase and continuous phase velocities, respectively.

The non-dimensional elasticity parameter \(\beta\), a measure of the degree of surface contamination, is defined as

\[
\beta = \Gamma_{eq} \frac{RT}{\sigma_o} = \frac{Q}{4\pi\tilde{a}^2} \frac{RT}{\sigma_o}, \quad \text{where} \quad Q = \int_S \Gamma dS, \tag{5.1}
\]

where \(\Gamma\) is surfactant concentration, \(\sigma_o\) signifies clean-drop surface tension and equilibrium (eq) is defined as the case of uniform surfactant concentration on a spherical drop. We assume a linear equation of state \(\sigma = \sigma_o - RT\Gamma\), where \(R\) is the universal gas constant and \(T\) the uniform absolute temperature. The equilibrium surface tension can then be expressed as

\[
\sigma_{eq} = \sigma_o(1 - \beta). \tag{5.2}
\]

The nondimensional velocity and length are scaled differently for the boundary-integral formulation presented in the following section vs. the numerical results in §5.4, so these parameters as well as the capillary number \(Ca\) are provided in their respective sections.
Figure 5.1: Initial configurations of the periodic emulsion (cyan) and solid phase (translucent gray). One repeat unit cell shown. Characteristic length $L$ is the dimension of the cubic cell, and $\tilde{a}$ and $\tilde{a}$ are the radii of the solid sphere and non-deformed droplet, respectively. Surfactant concentration not shown. Insets show the view along any one of the axes. (a) The system for an emulsion concentration $c_{em} = 0.36$ begins with an initially spherical droplet. (b) The droplet for $c_{em} = 0.5$ does not fit in the pore in a non-deformed (spherical) state, so the initial drop shape is created by swelling from a spherical drop of smaller radius.

5.3 Boundary-integral formulation for periodic contaminated emulsions

The Hebeker representation is used for each solid-particle contribution as a linear combination of single-layer and double-layer potentials, and the interfacial stress contribution is desingularized for both drop self-interactions and drop-solid contributions. The resulting Fredholm integral equations of the second kind are well-behaved for tight-squeezing drops, for which drop-solid separation distances can be several orders of magnitude smaller than the system’s characteristic length. The velocity and length scales are made nondimensional using $(\nabla p)\tilde{a}^2/\mu_e$ and $L$, respectively (within this section only). As presented in Zinchenko & Davis (2008b), the formulation uses Hasimoto’s periodic Green’s functions $G^{(k)}(x)$ ($k = 1, 2, 3$) and the corresponding stress tensors $\tau^{(k)}(x)$. At every time step the following system of equations is solved for continuous phase velocity $u^e$ at the drop surface, with the Hebeker density $q$ on
solid surfaces:

\[ u^e(y) = F(y) + (\lambda - 1) \int_S Q(x) \cdot \bar{\tau}(r) \cdot n(x) \, dS_x \]

\[ + \int_S Q(x) \cdot [\eta G(r) + 2\bar{\tau}(r) \cdot n(x)] \, dS_x \]

\[ + \int_{\hat{S}} q'(x) \cdot [\eta G(r) + 2\bar{\tau}(r) \cdot n(x)] \, dS_x + C \quad (5.3) \]

for \((y \in \hat{S})\). Here, \(r = x - y\), \(n\) is the unit normal to a surface, \(\eta > 0\) is the Hebeker parameter (the choice of \(\eta\) affects the algorithm robustness, but not the solution upon numerical convergence), and prime indicates rigid-body projection. The fluctuations \(Q(x)\) are defined as \(u - u'\) on the drop and \(q - q'\) on the solid surface. The fully symmetric third-rank tensor \(\bar{\tau}\) corresponds to the periodic part of the fundamental stresslet:

\[ \bar{\tau}^{(k)}_{ij}(r) = \tau^{(k)}_{ij}(r) - r_k \delta_{ij}. \quad (5.4) \]

The inhomogeneous term is

\[ F(y) = \frac{1}{|\langle \nabla p \rangle| \alpha^2} \int_S f(x) \cdot G(r) \, dS_x, \quad (5.5) \]

with

\[ f(x) = 2\sigma(x)k(x)n(x) - \nabla_s \sigma \quad (x \in \hat{S}), \quad (5.6) \]

where \(\nabla_s\) is the surface gradient and \(k\) is the mean surface curvature \(k(x) = (k_1 + k_2)/2\), with \(k_1, k_2\) being the principal curvatures at \(x\).

Equation (5.3) is used to find \(q(x)\) on the solid and \(u(x)\) on the drop by taking the limits \(y \to \hat{S}\) and \(y \to \tilde{S}\), respectively. Finally, the unknown constant \(C\) is excluded from (5.3) by substituting the
equation for $q(x)$ into the nondimensional force balance:

$$\eta \int_S q(x) \, dS_x = (L/\tilde{a})^2 e_z. \tag{5.7}$$

After desingularization of droplet-droplet, droplet-particle, and particle-particle interactions, including the Marangoni contribution tangential to the drop surface, the system of equations (5.3) is solved by GMRES iterations. Drop node positions are time-integrated using a simple Euler time-marching scheme, with an adaptive time step that incorporates the maximum curvature of the drop surface. Simulation times are greatly reduced through the use of multipole acceleration. The surfactant is advected using an upwind finite-volume scheme. Mesh quality is maintained using both passive mesh and active stabilization. Further details can be found in Zinchenko & Davis (2008a), Zinchenko & Davis (2008b) and Gissinger et al. (2019a).

### 5.4 A contaminated emulsion squeezing between spheres: numerical results

Within this section, the nondimensional velocity and time are scaled differently than above, with considerations for the (low) single-phase fluid velocity flowing through the dense cubic lattice used herein. Velocities are scaled with $|\langle \nabla p \rangle| \tilde{a}^2 / (45 \mu_e)$, and time with $45 \mu_e / |\langle \nabla p \rangle| \tilde{a}$. The factor of 45 comes from the average single-phase velocity estimated by the Carman-Kozeny equation at 50% solid fraction. The capillary number is defined as $Ca = |\langle \nabla p \rangle| \tilde{a} / \sigma_{eq}$. Surface tension and surfactant concentration at the drop surface are scaled with their equilibrium values, where equilibrium (eq) is defined as the case of uniform surfactant concentration on a spherical drop:

$$\Gamma^* = \Gamma / \Gamma_{eq}, \quad \sigma^* = \sigma / \sigma_{eq}.$$ 

For the entirety of this section, the superscript * will be dropped for conciseness.
5.4.1 Contaminated high-density emulsion squeezing

A contaminated train of droplets flowing through a periodic array of spheres quickly reaches a regular periodic cycle, as was observed for a clean emulsion (Zinchenko & Davis, 2008b), but in this case both in terms of drop motion and surfactant distributions. Several snapshots during this cycle for $c_{em} = 50\%$ are shown in figure 5.2, where the starting time $t_T = 0$ was chosen arbitrarily, long after regular motion having a period of $T = 4.05$ was achieved. For continuity, it is helpful to focus on a consistent periodic image of the drop throughout the sequence, which corresponds to the top, middle, and bottom droplets, for $t_T = 0$, 1.5, and 2.8, respectively. The first frame is near the maximum drop velocity, after the drop has almost fully coated the solid particles and is being pushed into the next pore. Similar to single-drop squeezing in a far-field flow, sharp surfactant gradients can develop, with depleted regions wherever there are near-contact lubrication layers. In this case, film drainage also occurs between periodic images of the drop, resulting another depleted region within drop-drop near-contact regions (only two periodic images of the droplet are shown for $t_T = 0$ and $t_T = 2.8$). In contrast to single drops in far-field flow, the droplet phase moves faster than the carrier fluid (see figure 5.3), at least away from (and above) the critical capillary number for trapping. So, surfactant is swept toward the trailing end of the drop, and remains almost entirely confined to the trailing half throughout its periodic cycle. The most success that Marangoni stresses achieve in redistributing surfactant is near the droplet’s maximum velocity, where a small amount is pulled downstream, on the drop surface near the interparticle interstices. The drop near its minimum velocity is shown at $t_T = 1.5$ in figure 5.2, where it is nearly centered within the pore, and has ‘detached’ from the previous layer of solid particles and formed a lubrication layer between itself and the next layer of particles. Observing the near-zero concentration of surfactant on the leading half of the drop at this point ($t_T = 1.5$), Marangoni stresses clearly do not play a role in the initial formation of the lubrication layer with the next layer of particles. However, shortly thereafter, as seen at $t_T = 2.8$, surfactant is advected toward these near-contact regions, allowing Marangoni stresses to affect the thin-film dynamics and drainage.

The period of motion for the droplet, at this low degree of contamination $\beta = 0.05$, is notably higher than for a clean drop. As shown in figure 5.3, the period increases $>10\%$ from 3.63 to 4.05. In reference to figure 5.2, the initial frame $t_T = 0$ corresponds to $t = 3.5 + nT$, for integer $n$. The droplet phase velocity,
Figure 5.2: Snapshots of a pressure-driven contaminated droplet train flowing through a model porous media ($C_a = 1.27, \beta = 0.05, \lambda = 4, c_{em} = 0.5$). The initial snapshot corresponding to $t_T = 0$ was chosen arbitrarily, after regular periodic motion had been achieved with a period $T = 4.05$. For $t_T = 0$ and $t_T = 2.8$, all but two periodic images of the droplet are hidden. Only portions of the spherical solid particles (translucent gray) within one unit cell (black lines) are shown.

for both clean drops and $\beta = 0.05$, is significantly higher than that of the emulsion phase, especially at the maximum drop velocity when the drop is near-centered in the pore throat. One candidate for the disparity in period of motion is a change in lubrication behavior, i.e., different thin-film dynamics and general immobilization of the interface due to resistive Marangoni stresses. Such a possibility is evidenced by a distinct difference in the drop-particle separation throughout the squeezing process. As discussed by Zinchenko & Davis (2008b), there is a strong tendency for (extremely small) portions of the clean droplet to overlap with the solid particles, due to the difficulty of exactly solving the problem. This numerical challenge was overcome by introducing an artificial parameter $\delta_{min} \ll \hat{a}$, which prevented the drop surface from nearing within $\delta_{min}$ of the solid surface. However, this mechanism, with $\delta_{min} = 0.009\hat{a}$, was never triggered for the surfactant-laden drop ($\beta = 0.05$). Indeed, the drop-solid gap, which reaches a minimum slightly before the maximum drop velocity, remains above 0.01 for the duration of the squeezing cycle. The increased mesh stability is particularly helpful for contaminated drops, for which local deformations in the mesh can have adverse effects on the numerical surfactant-transport scheme. Another contributor of the slower period of motion could be related to the Marangoni flow, i.e., changes in the surrounding flow field.
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Figure 5.3: Comparison of drop (solid curve) and emulsion (dashed curve) velocities for clean ($\beta = 0$) vs. lightly contaminated ($\beta = 0.05$) emulsions flowing through a periodic array of spheres ($Ca = 1.27, \lambda = 4, c_{em} = 0.5$). The presence of a small amount of surfactant on the drop surface results in a longer period of motion.

driven by the surface tension gradients. For example, Pak et al. (2014) discussed the surfactant-induced migration of a viscous drop in Poiseuille flow (see figure 2 therein for a simple schematic of this phenomenon). So, in a quiescent fluid, a drop with any of the surfactant distributions shown in figure 5.2 would propel itself as Marangoni stresses redistributed its surfactant, in a direction corresponding to ‘upstream’ in the current problem.

5.4.2 Capillary number

The effect of capillary number $Ca$ on drop velocity is shown in figure 5.4. As expected, the period of motion $T$ increases with decreasing $Ca$, as surface tension forces increasingly resist droplet deformation and so slow drop squeezing pores. For clean drops, the average drop-phase velocity $U_D$ also decreases with capillary number (Zinchenko & Davis, 2008b). This trend holds for contaminated drops as well, though it is interesting to note that the maximum $U_D$ also increases with decreasing $Ca$. In other words, the drop resists moving through the pore throat for a longer time, but then ‘pops’ into the pore at
Figure 5.4: The effect of capillary number on contaminated emulsion squeezing ($\beta = 0.05, \lambda = 4, c_{em} = 0.5$).

(a) Period of motion increases with increasing $Ca$, as do the extrema of the drop velocities $U_D$ throughout the squeezing cycle. (b) A linear relationship is observed for $Ca$ vs $1/T^3$, and the extrapolated value of $Ca$ at the $x$-intercept is shown.

relatively-high velocity. It was also established for clean drops that the $Ca$ and $1/T^3$ are linearly related, suggesting that the critical capillary number, $Ca_{crit}$, below which droplets become trapped, can be extrapolated as $T \to \infty$. This relationship holds in the case of a contaminated emulsion, at least away from critical conditions, as shown in figure 5.4 for $\beta = 0.05$. This would result in $Ca_{crit} \approx 0.74$, barring any deviation from this linear relationship near critical conditions (see §5.4.4 for a discussion of why such a deviation could occur in the case of contaminated drops). For a clean emulsion $Ca_{crit} \approx 0.68-0.70$ (Zinchenko & Davis, 2008b), corresponding to $>5\%$ increase in the extrapolated $Ca_{crit}$ after introducing a small degree of contamination. For single-droplet squeezing in far-field flow, incremental increases in the degree of contamination were seen to decrease squeezing times, which was attributed to an increase in local deformability as surfactant accumulated at the leading tip of the drop. The inverse trend (see next subsection) for confined periodic squeezing is attributed to the very different surface-distribution of surfactant throughout the squeezing cycle. With a near-zero concentration of surfactant on the leading half of the droplet, where a local increase in deformability seems most beneficial for squeezing, the relative immobilization of the interface is instead the dominant dynamic.
5.4.3 Degree of contamination

Increasing the degree of contamination on the drop surface from low ($\beta = 0.05$) to moderate ($\beta = 0.1$) further increases the period of motion from 4.05 to 4.43, as shown in figure 5.5a, an increase only slightly less than the increase from $\beta = 0$ to $\beta = 0.05$. The curves, otherwise similar, are also consistently shifted downward to lower $U_D$ with increasing degree of contamination. The continuation of these trends is attributed to the incremental increase in the strength of the factors discussed above (e.g., Marangoni stresses resisting surface mobility). A persistent concern when simulating insoluble surfactant is that too much surfactant could build up in one localized area, since the surfactant cannot desorb from the interface. As with a single drop in far-field flow, the linear equation of state was used herein with the assumption that linearization of the Langmuir-Szyszkowski equation is valid when $\Gamma_{eq} \ll \Gamma_{\infty}$, where $\Gamma_{\infty}$ is the maximum surfactant coverage corresponds to a monolayer (see Gissinger et al. (2019a), §2 therein). Follow-up work explored a non-linear relationship between surfactant concentration and surface tension, and confirmed that using the Langmuir equation of state did not significantly affect drop squeezing behavior, with respect to that single-drop system (unpublished). The variations in the maximum surfactant concentration for $\beta = 0.05$ and $\beta = 0.1$ are shown in figure 5.5b. The metric $\Delta(\beta \Gamma_{max}) = \beta \Gamma_{max} - (\beta \Gamma_{max})_{eq}$ is scaled by the elasticity parameter $\beta$ to allow for direct comparisons of the relative increase in surfactant concentration. The maximum value of $\Delta(\beta \Gamma_{max})$ in figure 5.5b is very close to that observed for near-critical single drops in far-field flow, indicating that a similar justification of the linear equation of state holds. A value of $\Delta(\beta \Gamma_{max}) = 0.4$ corresponds to $\approx 40\%$ decrease from the equilibrium surface tension.

5.4.4 Emulsion concentration

The surfactant behavior for an emulsion of moderate concentration ($c_{em} = 36\%$) is qualitatively similar to that of the higher-density emulsion ($c_{em} = 50\%$) discussed above. The snapshots shown in figure 5.6 are taken after the drop has settled into regular periodic motion, with $t_T = 0$ corresponding to a point in the cycle near the maximum drop velocity. The most obvious difference between $c_{em} = 36\%$ and $c_{em} = 50\%$ is the greater droplet separation (between periodic images) that occurs when the drop is near the center of
Figure 5.5: Effect of increasing degree of contamination on drop-phase emulsion dynamics \((Ca = 1.27, \lambda = 4, c_{em} = 0.5)\). (a) Increasing degrees of contamination from \(\beta = 0, 0.05, \text{ and } 0.1\) corresponds to increasing periods of motion 3.63, 4.05, and 4.43, respectively. (b) Evolution of surfactant concentration with respect to contamination. For direct comparison, \(\Gamma_{max}\) is scaled by \(\beta\) and shifted by \((\beta \Gamma_{max})_{eq}\).

The pore \((t_T = 1.24)\). The capillary number 0.995 is away from the (substantially lowered) critical capillary number for this droplet size, so the significantly reduced period of motion \(T = 2.79\) compared to those of the \(c_{em} = 50\%\) emulsion with similar parameters is not surprising. It is noteworthy, though, that the droplet must still undergo large deformations to pass through the pore throat, and almost fully coat the solid particles in a similar fashion.

As shown in figure 5.7, the droplet phase velocity increases (and therefore the period of motion decreases) for this moderate-density emulsion \(c_{em} = 36\%,\) compared to \(c_{em} = 50\%\) (cf. figure 5.3). However, as can be inferred from the surfactant distribution, the drop-phase velocity remains significantly higher than the continuous phase (see figure 5.7). Considering that the droplet must nearly coat the solid particles for both moderate- and high-density emulsions, no significance difference in the relative drop- and emulsion-phase velocities is expected between these two densities. With respect to figure 5.6, the initial frame \(t_T = 0\) corresponds to \(t = 4.88 + nT,\) for integer \(n\).

A successful near-critical simulation of a moderate-density, unit-viscosity-ratio emulsion suggests
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Figure 5.6: Squeezing behavior and surfactant distribution for a lower-density emulsion \((c_{em} = 0.36)\) flowing through an array of spheres \((Ca = 0.995, \beta = 0.05, \lambda = 4)\). The period of motion is \(T = 2.79\).

Figure 5.7: Drop- and emulsion-phase velocities for the moderate-density emulsion flow \((c_{em} = 0.36)\) pictured in figure 5.6 \((Ca = 0.995, \beta = 0.05, \lambda = 4)\).
that deviations from the linear $Ca$ vs. $1/T^3$ relationship occur very close to critical squeezing conditions (figure 5.8a). For clean emulsions, it was noted that the drop-phase velocity remains above that of the continuous phase even relatively close to critical conditions, but that this trend must eventually invert when the emulsion nears (or falls below) the critical $Ca$ (Zinchenko & Davis, 2008b). This behavior is confirmed for a near-critical, but still supercritical, contaminated emulsion, as shown in figure 5.8b. For clean drops, there is no reason to believe that this inversion would invalidate the extrapolation of sufficiently supercritical behavior to obtain $Ca_{crit}$. However, for contaminated drops, the surfactant distribution is predicated on these relative velocities, and a qualitative difference in surfactant behavior, and therefore squeezing behavior, is expected. As shown in figure 5.8c, the surfactant is swept to the leading tip of the drop during a portion of the squeezing cycle, unlike for away-from-critical squeezing. This surfactant distribution resembles that observed for single drops, for which the presence of surfactant decreased $Ca_{crit}$. For clean emulsions, a critical capillary number $Ca_{crit} = 0.44$ was reported for this system (Zinchenko & Davis, 2008b). As shown in figure 5.8a, the extrapolated value of $Ca_{crit} = 0.47$ using away-from-critical values appears to be overestimated by at least 8%. Note, however, that simulation results become more sensitive to mesh resolution very close to critical squeezing conditions, and so additional convergence testing of this near-critical behavior is in order (and in progress).

### 5.5 Remarks on contaminated emulsions flowing through porous media

A periodic emulsion covered in insoluble surfactant flowing through a cubic array of spheres is simulated using the boundary-integral method, by considering a one-drop, one-particle repeated unit cell. The close approach of fluid interfaces to each other and to solid surfaces is resolved using a suite of desingularization tools, and simulations are greatly sped up using multipole acceleration. A robust convection scheme for surfactant ensures stability of the simulation despite sharp concentration gradients that develop throughout the squeezing process. The emulsion consists of Newtonian fluids at small Reynolds number, and the drop surface tension is related to the local surfactant concentration by a linear equation of state.
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Figure 5.8: Very-near-critical squeezing of a moderate-density emulsion ($\beta = 0.05$, $\lambda = 1$, $c_{em} = 0.36$). (a) Away from critical, a linear relationship between $Ca$ and $1/T^3$ is observed, however, deviations from this relationship occur very near to critical conditions. (b) Very near critical squeezing conditions, the drop phase moves slower than the continuous phase for the majority of the squeezing cycle ($T = 7.55$, $Ca = 0.43$). (c) Snapshots of drop squeezing for the near-critical $Ca = 0.43$. The surfactant is swept to the downstream half of the drop during part of the squeezing cycle ($t_T = 3.88$, shown from a different angle to reveal surfactant distribution).
The solid phase is nearly packed, i.e., nearly overlaps with its periodic image, and comprises 50% of the periodic cell. Two densities of emulsion are considered, 36% and 50% of the void space between particles, both of which represent macroemulsions with non-deformed drop sizes considerably larger than the pore throats. The emulsion is driven through the porous medium under a constant average pressure gradient, inducing major deformation of the droplet and non-uniformity of the surfactant distribution.

Contaminated droplets quickly achieve regular periodic motion within an array of spheres. Due to the droplet phase moving faster than the continuous phase, surfactant is swept upstream, and remains confined to the trailing half of the drop throughout the squeezing cycle. The presence of surfactant increases the period of motion $T$ compared to a clean emulsion, and incrementally increasing the degree of contamination from $\beta = 0.05$ to $\beta = 0.1$ again increases this period. This apparent inhibition of droplet motion is attributed to the slowing of lubrication-layer drainage in the presence of surfactant, noting that the droplet must form a new lubrication layer with the next layer of solid particles during every squeezing cycle. A linear relationship holds between $Ca$ and $1/T^3$ for contaminated drops away from critical conditions, but deviations from this relationship are expected very near to critical conditions due to the redistribution of surfactant when the drop-phase velocity drops below the continuous-phase velocity. A low degree of contamination significantly increases squeezing times as compared to clean droplets, an inverse trend to that observed for a single drop suspended in uniform far-field flow. The disparity is attributed to the very different surfactant distributions between confined vs. isolated systems. Decreasing the density of the emulsion from 50% to 36% decreases the droplet period of motion, but qualitatively similar surfactant dynamics are observed between these two emulsion densities.

In addition to a more extensive study of the above systems, including investigation of lower viscosity ratios and higher surfactant concentrations, the tools developed herein will be applied to multidrop-multiparticle simulations. In particular, simulations of contaminated emulsions similar in scale to those completed by Zinchenko & Davis (2013), with up to 100 drops and 36 particles, should be feasible. One particular challenge when considering surfactant dynamics is droplet breakup. Furthermore, the possibility of daughter drops having a significantly different surfactant concentration, and therefore capillary number, compared to the original drops results in particularly rich local and global dynamics.
Chapter 6

Concluding remarks and recommendations for future work

The worst thing you can do is to completely solve a problem.

-Daniel Kleitman

6.1 Concluding remarks

6.1.1 Dissertation synopsis

Contaminated and confined emulsions are a complex but commonly-encountered system, fundamental understanding of which stands to benefit the fields of enhanced oil recovery, biotechnology, and the food and beverage industry. Several new formulations of the boundary-integral method, a powerful computational fluid dynamics tool, were presented herein that enable the high-accuracy investigation of droplets and emulsions interacting with complex solid phases and surfactants. The physics of these systems depend on several coupled physical phenomena, including viscous forces and surface tension, lubrication layer formation and drainage, and surfactant effects such as local decreases in surface tension and Marangoni stresses. These combined physics are challenging to address numerically, due to the close
approach of fluid-fluid interfaces to solid surfaces, development of high surfactant-concentration gradients
during tight-squeezing, and the sensitive behavior of numerical calculations near critical squeezing
conditions. These obstacles were overcome by introducing a multimesh desingularization method to allow
droplet interaction with arbitrary shapes, as well as a faster semi-analytical alternative for axisymmetric
shapes, several adaptive mesh resolution schemes, and several upwind-biased convection schemes for
surfactant transport. The behavior of drops squeezing between cylindrical objects, flat plates, and more
complex non-axisymmetric shapes was characterized, and the internal circulation and mixing of trapped
drops in those systems was visualized and quantified. Isolated surfactant-laden droplets squeezing between
spheres were modeled under a wide range of fluid and surfactant properties, as was surfactant-laden
emulsions flowing through a periodic array of spheres. Several new modes of droplet-squeezing and
surfactant-transport behavior are predicted, and it is hoped that the numerical algorithms presented herein
prove useful to other researchers as well.

6.1.2 Droplets and arbitrarily-shaped smooth obstacles

In chapter 2, it was demonstrated that arbitrarily-shaped smooth solid surfaces can be incorporated into
fully three-dimensional multiphase boundary-integral techniques. Previously, such a proposition was
considered untenable due to the requirement of analytical solutions for the solid-phase single- and
double-layer contributions used to desingularize drop-solid interactions. This extension was enabled by
introducing the multimesh desingularization method, which combines a hierarchy of embedded mesh
resolutions and a suite of desingularization tools to calculate surface integrals with high accuracy. In
addition, a more efficient semi-analytical method was introduced for axisymmetric particles such as
capsules. In addition to these tools, several adaptive meshing schemes for the drop interface were developed
to resolve droplet interactions with high-curvature surfaces. It was found that drop squeezing was greatly
inhibited by capsules even of small aspect ratio, as compared to spheres. The behavior of drop squeezing
between capsules does not converge with capsule length, up to lengths 20 times the drop radius, which
is attributed to a manifestation of the Stokes paradox. Results for a single drop approaching a single
fibrous particle are presented, including full treatment of the lubrication layer. As the drop passes around
both sides of the fiber, a thin filament forms connecting the two lobes swept downstream, and the shape of this filament affects lubrication layer drainage. Drops squeezing between flat plates with high curvature is achieved, as well as between other non-axisymmetric shapes and constrictions. Rectifying droplet flow is demonstrated for non-axisymmetric constriction such as angled plates, where the drop passes through the constriction in one direction, but undergoes drop breakup when approaching from the opposite direction.

6.1.3 Internal circulation and mixing within trapped droplets

In chapter 3, the internal circulation and mixing of droplets trapped in two types of constrictions, one composed of three spheres and the other of two capsules, is considered. The internal velocity field is recovered from interfacial velocities by solving the internal Dirichlet problem, using a desingularized boundary-integral formulation. These internal flows are analyzed as dynamical systems, and the locations and types of interior fixed points in the flow are identified. For the two-capsule droplet, one attracting focus saddle and one repelling focus saddle interact to produce regular flow within the drop. For the three-sphere droplet, two attracting focus saddles are identified on symmetry planes of the droplet. Poincaré maps at the drop centre indicate chaotic advection within the three-sphere drop, which is associated with efficient mixing. The internal mixing is visualized using passive tracers and material lines to represent the interface between two dyes. An algorithm for advection of a material surface with arbitrary bounds is presented, and used to visualize the 3D flow within each droplet. The rate of growth of these surfaces, proportional to the topological entropy of the flows, also suggests the three-sphere droplet is more effective at mixing.

6.1.4 Surfactant-laden droplets squeezing through interparticle constrictions

In chapter 4, the behavior of surfactant-laden droplets embedded in a far-field flow and squeezing through a three-sphere constriction is considered. Extremely sharp gradients of surfactant concentration form on the drop interface during tight-squeezing, and it is found that upwind-biased convection schemes are required to stably resolve surfactant transport. Several non-diffusive convection schemes are implemented, including a robust upwind finite-volume method and a flow-biased least-squares method, and used in conjunction with a linear equation of state to describe the interfacial effects of surfactant over a range of
parameters. As compared to clean drops, the presence of surfactant affects the interfacial velocity field and lubrication behavior, and is found to decrease squeezing times as well the critical capillary number for trapping. This trend continues with increasing degree of contamination, up to a point above which there is negligible impact on squeezing dynamics. At low viscosity ratios, Marangoni stresses have a stronger effect, and can result in some surfactant being pulled back upstream during squeezing, and the drop exiting the constriction with a bimodal distribution of surfactant.

6.1.5 Surfactant-laden emulsions flowing through porous media

In chapter 5, emulsions covered in insoluble surfactant flowing through a cubic array of spheres are modeled. Droplets quickly achieve regular periodic motion, both in terms of droplet and emulsion phase velocities, and in terms of surfactant distribution, characterized by a period of motion $T$. Except very near to critical squeezing conditions, droplets travel faster than the continuous phase, resulting in the vast majority surfactant being swept to the upstream half of the droplet for the duration of the squeezing cycle. In contrast to isolated single drops, the presence of surfactant increases drop squeezing times, which is attributed to the Marangoni effect slowing lubrication layer drainage. Away from critical conditions, the $Ca$ vs. $1/T^3$ obeys a linear scaling, as was observed for clean drop, and which would predict an increase in $Ca_{crit}$ due to the surfactant-inhibited drop motion. However, this scaling breaks down near critical conditions since very-near-critical droplets can move slower than the carrier fluid, eventually sweeping surfactant to the leading tip of the drop and enabling pass-through.

6.2 Suggestions for future work

A number of interesting directions for future research come to mind, both in terms of the directly extending the work outlined in each chapter herein, and in terms of combining these related but distinct topics. In the case of drop flow between arbitrary shapes, there arises the question of which shape to try next. Perhaps the most pertinent suggestions in this regard come from experimentalists: based on conversations with microfluidic researchers, it is of interest to identify the fluid properties that cause drop
breakup when the drop is forced through a given periodic constriction. This apparently simple request would involve several extensions to the current code, including support for complex shapes in periodic cells as well as allowing for those simulations to continue post-breakup. One particularly interesting configuration is a rectangular grid, which could be used to demonstrate emulsification via a membrane, and could be efficiently achieved with a combination of the multimesh and semi-analytical desingularization methods. With respect to surfactant-covered drops, it is of interest to comprehensively investigate the effect of non-linear equations of state (preliminary work suggests that they have little effect on droplet dynamics in comparison to the linear equation of state).

Finally, the capabilities introduced in the first three chapters are mutually orthogonal, so combining them could reveal interesting new physics. For example, the internal mixing visualization and analyses applied to stationary drops could be applied to periodic emulsions. Preliminary efforts to combine the complex shape and surfactant codes have begun, in order to answer questions such as ‘what is the effect of surfactant on drops squeezing through fibers?’ Similarly, it would be interesting to investigate both clean and surfactant-covered droplets flowing through a bed of non-spherical particles.


